

FE--0496-176

DE81 008082

SOLVENT REFINED COAL (SRC) PROCESS

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD
JULY, 1979 THROUGH SEPTEMBER, 1979

THE PITTSBURG & MIDWAY COAL MINING CO.
Denver, Colorado 80222

February 1980

PREPARED FOR THE
U. S. DEPARTMENT OF ENERGY
DIVISION OF COAL CONVERSION AND UTILIZATION
UNDER CONTRACT DEAC-0179-ET10104
(formerly EX-76-C-01-0496)

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

T A B L E O F C O N T E N T S

	<u>Page No.</u>
I. SUMMARY	2
II. PILOT PLANT OPERATIONS, ENGINEERING, AND MAINTENANCE . . .	3
A. Coal Receiving and Slurry Preparation (Area 01) . . .	3
B. Slurry Preheating and Dissolving (Area 02)	5
C. Mineral Separation and Recycle Process Water (Area 03). . .	7
D. Solvent Recovery (Area 04)	9
E. Gas Compression and Naphtha Unit (Area 05)	12
F. Product Solidification (Area 08)	12
G. Process Waste Disposal (Area 09.1)	12
H. Tank Farm (Area 09.2)	13
I. Gas Systems (Area 09.5)	13
Inert Gas Unit	13
Hydrogen Unit	13
J. Dowtherm (Area 09.8)	14
K. Lummus Deashing Project (Area 10)	14
III. PILOT PLANT PROCESS ANALYTICAL DATA	15
IV. PILOT PLANT SPECIAL STUDIES	16
A. Short Residence Time SRC-II Test	16
B. SRC-I Process Solvent Inventory	17
C. Lummus Deashing Unit	17
D. Rheological Study	19
E. Vacuum Flash Test Stand	24
F. Dissolver Mixing Study	25
G. Lawrence Pump Performance	26
H. Pressure Control Valve Performance	29
I. Outside Studies	32
V. HARMARVILLE PROCESS DEVELOPMENT UNIT P-99	33
A. SRC-II Operation Process Development Unit P-99	33
B. Hydrotreating of SRC-II Naphtha	35
C. Vacuum Column Operation	35
D. Future Plans	40
APPENDIX A - SRC Pilot Plant Tables and Figures	41
APPENDIX B - Process Development Unit P-99 Tables and Figures	66

T A B L E O F C O N T E N T S

Page No.

APPENDIX C - Chemical Analysis and Leaching of Coal Conversion Solid Wastes	89
APPENDIX D - Mossbauer Spectroscopic Studies of the Mineralogical Changes in Coal as a Function of Cleaning, Pyrolysis, Combustion and Coal Conversion Processes	104
APPENDIX E - Identification of Potential Pollutants From Coal Conversion Wastes	130
DISTRIBUTION LIST	139

LIST OF TABLES

<u>Table No.</u>		<u>Page</u>
A-1	Coal Processing Summary	42
A-2	Average Raw Coal Analyses, Wt%	43
A-3	Average Dried, Pulverized Coal Analyses, Wt%	43
A-4	Average Analyses For Forms of Sulfur, Wt%.	43
A-5	Average Sieve Analysis of Dried, Pulverized Coal, Wt%	44
A-6	Typical Analysis of Stripper Bottoms, Wt%	44
A-7	Average MAF Coal Conversion, Wt%	45
A-8	Average Fractional Analyses of Liquid Products	45
A-9	Average Analysis of Pilot Plant Vacuum Bottoms, Wt%	46
A-10	Typical Analysis of Lummus Unit Vacuum Bottoms, Wt%	46
A-11	Process Waste Disposal Analyses	47
A-12	Analyses of Selected Lummus Samples	48
A-13	Lafayette Mine, Kentucky No. 9 Coal Proximate and Ultimate Analyses	49
A-14	Lafayette Mine, Kentucky No. 9 Coal Maceral Analyses	50
A-15	Short Residence Time SRC-II Test Reaction Conditions	51
A-16	Short Residence Time SRC-II Test Estimated Product Yields.	52
A-17	Limitations On Rotovisco Operating Range	53
A-18	Actual and Predicted Effects of Solids On Slurry Viscosity	54
A-19	Comparison of Composition and Viscosity of 208 Samples	55
A-20	Reaction Area Transit Time For Radioisotope Tracer Injections	56
B-1	Properties of Fourth Shipment of Powhatan No. 5 Mine Coal (LR-26982)	67
B-2	Operating Conditions for Runs 56 and 57 Made in PDU P-99	68
B-3	SRC-II Yields for Runs Made on PDU P-99	69
B-4	Inspections for SRC-II Naphtha Feedstock	70
B-5	P-99 Vacuum Column Operation	71
B-6	Viscosity of Vacuum Tower Bottoms 475°F	72
B-7	Viscosity of Vacuum Tower Bottoms 500°F	73
B-8	Viscosity of Vacuum Tower Bottoms 525°F	74
B-9	Viscosity of Vacuum Tower Bottoms 550°F	75
B-10	Viscosity of Vacuum Tower Bottoms 575°F	76
B-11	Viscosity of Flash Tower Bottoms for Run P-99-55	77
B-12	Properties of Vacuum Tower Bottoms	78
B-13	Emission Spectrographic Analysis of Fractionator Bottoms	79
B-14	Emission Spectrographic Analysis of Vacuum Tower Overhead	80

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
A-1	SRC-I Solvent Inventory.	57
A-2	Limitations on Rotovisco Operating Range	58
A-3	Comparison of Experimental Data and Estimates for Solids Effect on Viscosity in Artificial Slurry	59
A-4	Torque Error Introduced by Magnetic Drive Probe .	60
A-5	Comparison of Corrected Magnetic Drive Probe Data With Viscosity Standard Data	61
A-6	Letdown Valve Position, Flow Rate, Pressure Differential vs. Time	62
A-7	Fisher Valve Trim Assembly (LCV-166A)	63
A-8	Willis Valve Trim (LCV-166B)	64
A-9	Letdown Valve Trim Position, Flow Rate, Pressure Differential vs. Time	65
B-1	P-99 Vacuum Column	81
B-2	Viscosity vs. 1/T (Absolute)	82
B-3	VTB Viscosity vs. Flash Zone Temperature	83
B-4	Flash Zone Temperature vs. % Distillate in VTB .	84
B-5	VTB Viscosity vs. % Distillate in VTB	85
B-6	Vacuum Column Feed Distillation Curve for Period P99-54-11	86
B-7	Vacuum Column Feed Distillation Curve for Period P99-54-121	87
B-8	Vacuum Column Feed Distillation Curve for Period P99-55-1.	88

ABSTRACT

This report summarizes the progress of the Solvent Refined Coal (SRC) project by the Pittsburg & Midway Coal Mining Co. for the Department of Energy for the period June 25, 1979 through September 30, 1979. Except for brief periods, the Fort Lewis Pilot Plant continued to operate in the SRC-I mode and to process Kentucky No. 9 and 14 coal from Pittsburg & Midway's Colonial Mine. Testing of the Lummus Antisolvent Deashing Unit resumed July 21 and continued to operate through August 20, but prolonged steady state operation was not achieved. The Pilot Plant was shutdown August 25 to complete the installation of the new preheater in Area 02, for annual inspection, for conversion to SRC-II mode operation, and for extensive modifications to Areas 01 and 04. Operation is scheduled to resume the week of October 12 in the SRC-II mode to test the new Area 02 preheater.

Process Development Unit P-99 was down during July for the annual summer turnaround. Returning to lined out conditions on coal after the turnaround was delayed by a series of equipment failures. After these problems were overcome, two runs (Runs 56 and 57) were completed during the third quarter. These runs, made on Powhatan No. 5 Mine coal, showed that C₅-900°F distillate yield increased about 5% as pressure was increased from 2000 to 2500 psig.

I. SUMMARY

The major activities at the Fort Lewis Pilot Plant during the third quarter of 1979 were testing of the Lummus Antisolvent Deashing Unit and planning for the annual shutdown.

Because of a train derailment in Washington state and shipment delays at Colonial Mine, the Pilot Plant inventory of this coal became severely depleted and Kentucky No. 9 coal from Lafayette Mine was introduced on July 6 in order to stay on stream. When unrelated problems caused interruption of feed to the Lummus Unit, Powhatan No. 5 coal was introduced in the SRC-II mode in an effort to increase severely depleted process solvent inventory.

The third Lummus Deashing Unit run was begun on July 21 and extended through the end of the month. During this run, all six individual underflow control valves were kept fully open and automatic flow metering and control was maintained on the combined underflow stream only. Each individual stream was periodically tested to determine if a no-flow condition existed. This mode of control significantly reduced the underflow plugging problems experienced in earlier runs. After a few days of high overflow ash concentration, the unit began producing specification overflow product (less than 0.05% ash) on July 29.

The Lummus Unit was able to demonstrate sustained production of specification product only during two periods of operation from July 29 through August 10. The first period lasted 94 hours; the second period lasted 84 hours. During these periods, the overflow/underflow split was nominally 55/45. From August 10 through August 15, feed to the bottom compartment was stopped and fractionator bottoms were recirculated through the compartment to purge a suspected buildup of solids. Feed continued to be distributed to the top and middle compartment during this time, but overflow clarity was not on-spec. On August 17, a three day run was started to determine the operability of the unit using only the top and middle compartments of the settler with 60% of the feed going to the top compartment. The unit was able to produce specification product with an overflow/underflow of 63/37 from August 18 until 1000 hours August 20 when feed was discontinued.

The Fort Lewis SRC Pilot Plant was shut down August 25 for inspection, maintenance, modification, and conversion to SRC-II mode operation. Immediately prior to the plant shutdown, a special 80-drum shipment sample of process solvent with an initial boiling point of 550°F was prepared in Area 04 for use in a vacuum bottoms gasification run at Texaco, Montebello, California.

At the end of September, construction of Slurry Preheater B was proceeding on schedule. Field erection of piping was about 95 percent complete and hydrotesting, tracing, and insulation was continuing on available piping. Since Gray Tool was unable to supply the prototype high pressure isolation gate valves required

for the feed line tie-ins, a shutdown of the reaction area will be required to take Slurry Preheater B out of service for inspection.

As long as no unforeseen difficulties arise, maintenance activities at the Fort Lewis Pilot Plant will be completed and operations will resume during the week of October 21. At this time, Pittsburgh Seam coal from Powhatan No. 6 Mine will be processed in the SRC-II mode. Testing of the new slurry preheater and evaluation of the recent modifications in the slurry mixing area will be the primary short-term operating objectives.

During July, Process Development Unit P-99 was down for its annual summer turnaround. Examination of the unit at this time showed that it was in good condition and that relatively little coke had been deposited in equipment items. Getting back on stream at lined out conditions was delayed because of a number of equipment problems, such as high pressure leaks, and pump failures which leaked excessive amounts of pump flush oil into the slurry mix tank. When these problems were overcome, two run conditions, Runs 56 and 57, were successfully completed. Run 56 was made with a dissolver pressure of 2000 psig, average dissolver temperature of 851°F, nominal slurry residence time of one hour, and approximately 30 wt. % coal in the feed. Conditions for Run 57, were the same as for Run 56, except that the pressure was increased to 2500 psig. This work showed about a 5% increase in C₅-900°F distillate resulting from the pressure increase.

II. Pilot Plant Operations, Engineering, and Maintenance

A. Coal Receiving and Slurry Preparation (Area 01)

Coal processed during the reporting period June 25 through September 30, 1979, included 2157 tons of Kentucky Nos. 9 and 14 coal from Colonial Mine, 265 tons of Kentucky No. 9 coal from Lafayette Mine, and 190 tons of Pittsburgh Seam coal from Powhatan No. 5 Mine. The hourly onstream factor adjusted for downtime not directly caused by process problems or equipment failures, was 95.9%. A coal processing summary covering third quarter performance and overall process operating history is shown in Table A-1.

Colonial Mine coal was processed from June 25 until July 7 when operation was switched to Lafayette Mine coal in order to conserve Colonial coal for Lummus Unit testing. Conservation of the Colonial coal became necessary because of a train derailment in Washington state and procurement problems at the mine. Processing of Lafayette coal continued in the SRC-I mode until July 13 when operation was switched to partial recycle to improve the production of process solvent. Because of the apparent poor reactivity of Lafayette coal, feed was switched to Powhatan No. 5 coal and total recycle was substituted for partial recycle to increase process solvent yields and to build process solvent reserves. The use of Powhatan coal continued until July 18 when it was determined that additional shipments of Colonial coal would arrive before the

available inventory was depleted. Processing of Colonial Mine coal was resumed July 18 and continued through the third Lummus test run, as well as one additional day until the supply was depleted. Between August 22 and August 25, Powhatan coal was used to provide coal slurry for final processing of miscellaneous accumulated liquids. Processing operations were stopped August 25 to prepare the plant for the annual shutdown.

During the shutdown, work began on a major modification of the slurry recirculation system in Area 01. One of the objectives of this modification was to eliminate all deadlegs and restrictions which could cause plugging or accelerate erosion. Consequently, all of the piping in this system was redesigned and replaced. At the same time the piping specification was upgraded from 150 lb. to 300 lb. rating (G-1 to E-1). In addition, the suction piping on the high pressure charge pumps was redesigned to allow full recirculation flow through the suction chamber. Installation of a new hot flush solvent tie-in for the recirculation system was underway at the end of this period.

A second objective of the recirculation system modification was to increase the net positive suction head to the slurry circulation pumps. This was accomplished by raising the Slurry Blend Tank four feet and by repositioning the circulation pumps directly below the blend tank. A third objective was to install a Lawrence pump in place of one of the existing Durco pumps and to remove the remaining Morris pump from service. The Lawrence pump is being installed to evaluate its applicability in slurry service. Initially, a partially lined pump will be installed because a fully lined pump will not be available until February, 1980. Nevertheless, in the interim, the present pump will be sufficient to provide the necessary hydraulic data for scale-up. A new 6K Stellite quadrant edged orifice meter was installed in the recirculation line, not only to monitor the performance of the Durco and the Lawrence pumps, but also to define the minimum flow required to operate the vortex or eductor mix systems.

Repair of the carrier inert gas system was completed including inspection of the inert gas heater, replacement of the demister mat in the dehumidifier and overhaul of the inert gas blower. In the vortex mix system, the existing Teflon liner in the Slurry Mix Tank was replaced with a new stainless steel liner and the original 6" impellers were replaced with new 7" impellers. Changes to and repair of the coal delivery system consisted of installation of Pulsonic bin activators on the coal surge bin, replacement of the balls in the pulverizer, and overhaul of the rotary airlocks and the baghouse inert gas regulator system. New E-23 Nomex bags have been ordered for the baghouse, but they will not be available for installation until October 10.

B. Slurry Preheating and Dissolving (Area 02)

Except for approximately 79 hours of partial and total recycle operation that was utilized to increase process solvent inventory, all operation was in the SRC-I mode to make feed available to the Lummus Antisolvent Deashing Unit. Dissolver outlet temperature was 850°F except during short periods of Lafayette coal feed when the Lummus Unit was down for repairs. An 825°F dissolver outlet temperature was specified at these times to line out for a possible material balance run. This material balance run was not conducted during the reporting period, because repairs to the Lummus Unit were of short duration.

Dissolver pressure was adjusted several times during the period to meet varying operating requirements. Early in the reporting period the High Pressure Flash Drum level control valve (LCV-166A) was leaking even when fully closed. The differential pressure across the valve was reduced and an on-line stem travel adjustment was made. Flow was then controllable until June 28, when it was necessary to switch to the spare Willis control valve (LCV-166B). At that time, however, the first Willis block valve downstream of the High Pressure Flash Drum was plugged. After unsuccessful attempts to clear it with hydraulic pressures up to 3500 psig, the plug was partially cleared by placing the loop in service with a high differential pressure between the High and Intermediate Pressure Flash Vessels; LCV 166B was then used through the remainder of the operating period.

Pressure in the dissolver area was raised to various levels later in the reporting period to help increase the inventory of process solvent. It was raised to 2000 psig during raw solvent processing on July 18-19 and also during all periods of partial or total recycle operation. On August 22, it was necessary to lower the pressure to 1700 psig to control the flow through LCV-166B which was leaking excessively. During periods of normal SRC-I operation the target dissolver pressure was set at various values between 1600 and 1800 psig.

Because of other priorities, repair of LCV-166A was delayed. Finally, on July 10, when coal feed was stopped for other reasons, a new tungsten carbide seat and plug were installed on-line under reduced pressure of 1000 psig. The 1/4 inch Micro-Form trim which had been in service since March 30 was replaced with 1/4 inch taper-type trim. LCV-166A was held for stand-by service for the remainder of the operating period.

On July 13, a leak developed at the Slurry Recycle Stripper vapor fin-fan cooler. Repairs included installation of an alternate one inch vapor line for the stripper overhead, rolling of all tube ends, and pressure testing at 300 psig. Replacement tubes were ordered for installation during the August shutdown.

On July 14 a small leak of process material was noticed on the weephole of the inlet nozzle to the Intermediate Pressure Flash Vessel. This indicated that the interior nozzle breather ring or nozzle liner had developed a leak. The leak at the weephole was valved until the nozzle could be inspected internally during the annual shutdown.

Between August 25 and August 28, Area 02 vessels and piping were cleaned for inspection by flushing with process solvent followed by recirculating wash solvent. Vessels were then drained of oil and chemically passivated using established procedures.

During the shutdown a new ultrasonic flowmeter was installed in the feed line to the new slurry preheater. This meter was developed by Argonne National Laboratory. In order to use the transducers which were originally designed for low temperatures, two standoff rods were used to serve as wave guides so that the transducers could be isolated from the process heat. If this method of slurry flow measurement proves successful, ANL may be asked to design a high temperature transducer for installation and testing. ANL already has developed a transducer which operates at 900°F, but its frequency is too high for use with streams containing solids. Development of these new transducers would require approximately 7 months.

Additional work completed or in progress during the plant shutdown included the following:

Construction of Slurry Preheater B was on schedule and approximately 90% completed. Gray Tool was unable to supply the prototype high pressure isolation gate valves required for alternate operation with the existing preheater. Consequently, a spool piece will be used in their place until they are available.

Representatives of Gulf Science and Technology inspected Dissolver A, the High Pressure Flash Vessel, the Intermediate Pressure Flash Vessel, and the Recycle Condensate Separator. The nozzle breather rings on the head of the Intermediate Pressure Flash Vessel were showing signs of cracking. Though neither of the breather rings were completely cracked, they will be repaired to ensure safe operation. Inspection of the inlet nozzle of the Intermediate Pressure Flash Vessel to determine the cause of weephole leakage was in progress at the end of this quarter.

A metallurgical inspection of Area 02 was conducted to ensure that critical high pressure piping components were of 347 stainless steel construction as some materials certification problems have been experienced recently. Three 2" Grayloc hubs, one 4" Grayloc hub, one 2" tee, and one 2" block valve were found to be made of material

other than 347 stainless steel. The 2" hubs and valve were replaced with 347 stainless steel components. The 4" hub and 2" tee will be tested to determine if they are 321 stainless steel which would be acceptable.

A new flow transmitter (FT-144B) was installed and piping revisions made to measure the total hydrogen purge flow to the Slurry Preheater B pressure taps, the slurry charge pumps, and the dissolver quench minimum flow. FT-144A will now measure only the flow to the level taps on the Area 02 flash vessels and the Recycle Slurry Stripper.

Piping revisions around LCV-166 A and B (the pressure letdown valves of the High Pressure Flash Vessel) were completed. These revisions will eliminate deadlegs and reduce plugging problems encountered in this piping when switching from one valve to the other.

The Recycle Slurry Stripper overhead fin-fan cooler was removed and pressure tested. One tube was removed and the corresponding tube sheet holes were plugged. A new cooler will be ordered.

The installation of a smaller diameter erosion/corrosion test loop between the dissolver and the High Pressure Flash Vessel was complete except for heat tracing, insulation and the hookup of an on-line erosion monitoring system provided by Argonne National Laboratories.

C. Mineral Separation and Recycle Process Water (Area 03)

The high pressure water quench system caused a series of problems. These included blown packing and head gaskets on both the recycle water pumps, loss of control on the pressure control loop (PCV 1309) and a wire drawn seat on one water pump discharge pressure relief valve (PSV 1319). It is felt that the majority of these problems were caused by insufficient pressure on the discharge snubbers of both pumps. Special valves and gauges for monitoring snubber pressure have been ordered which should resolve the problem.

The Lawrence slurry pump which circulates the contents of the Filter Feed Surge Vessel was removed from service for repair on June 27. The bearing housing casting which was cracked between the cooling water jacket and the lube oil reservoir was repaired with epoxy. A new casting will be provided by the Lawrence Company since the original was defective. In addition, the partially lined casing was eroded in the volute section and was replaced. The new casing was hardened with a proprietary diffusion coating that should provide better protection against erosion than the spray coating used on the original.

Oil/water separation in the Recycle Process Water Tank (RPWT) was poor during July, particularly during periods of raw solvent feed. Although the exact mechanism of the emulsion formation in the RPWT is not completely understood, it may be caused by foaming in Area 02 during raw solvent runs or stripping of heavy solvents during start-ups. Emulsion formation in the RPWT causes feeding of large amounts of chloride saturated water to the fractionating columns and dumping of large quantities of oil, phenols, ammonia and sulfides to waste treatment. Studies were initiated to plot RPWT laboratory analyses and operating data, and to determine if any correlation between fractionating column corrosion and long term effects in waste treatment exists.

On July 23 a new line was installed between the Lummus Unit and the suction of the Filter Feed Flash Vessel recirculation pump so that the flash vessel could be used as a surge between the Lummus Unit and Vacuum Flash Drum B in Area 04. The addition of a double block valve and bleed at the Lummus Unit, on July 26, also made it possible to send either antisolvent-free underflow or antisolvent-free overflow to Vacuum Flash Drum B. Prior to the addition of these block valves only the underflow stream could be routed to this flash drum.

The partially lined Lawrence pump used for Filter Feed Surge Vessel recirculation was disassembled for inspection on August 28. After 1400 hours of service the diffusion coating of the 410 SS pump casing was found to be deteriorated in high turbulence areas. The Lawrence representative estimated that wear rate would accelerate rapidly once the diffusion coating (.005 thick) was breached. Radial heat cracks were found on the suction side shroud of the impeller. The Lawrence representative theorized that this cracking was caused by the impeller rubbing on the suction disc. Clearance between the impeller and front liner was initially set too closely. When the pump shaft expanded longitudinally on heat-up, the impeller was pushed into the suction disc. Upon reassembly, a new impeller and liners will be installed with the proper clearances as recommended by the Lawrence representative. The pump casing will be reinstalled, without modification, prior to startup in order to monitor further erosion and to determine its service life. The HC 250 liners and impeller showed negligible hydraulic wear from the slurry. The majority of the wear was from the impeller rubbing on the liner. A procedure was developed for measuring the wall thickness on the pump casing while the pump is hot, utilizing an ultrasonic tester. The minimum wall thickness was measured at 0.700 inches. Lawrence indicated that the pump should be discarded when the wall thickness is reduced to 0.375 inches. The hot measurements with the ultrasonic tester will be verified during shutdown. Periodic measurements will be taken of the casing wall thickness, so that the pump can be removed from service when wall thickness deteriorates to less than the recommended value.

During the shutdown the following additional work was completed in Area 03:

The Dowtherm exchanger recirculation loops for both the Filter Feed Flash Vessel (FFFV), the Filter Feed Surge Vessel (FFSV), and the transfer line between these vessels were replaced with 316 stainless steel. A new 6K Stellite quadrant edged orifice meter was installed in the FFSV recirculation loop.

The pulsation dampeners and the pressure controller on the high pressure water booster pumps were overhauled. Repair of these pulsation dampeners should reduce the frequency of head gasket failure on these pumps.

D. Solvent Recovery (Area 04)

The old vacuum flash system was used throughout July, to process coal slurry from Area 02 or from the Lummus Unit during its periods of operation. On July 27-30, when the antisolvent-free overflow and underflow streams from the Lummus Unit were processed separately, the underflow stream and part of the overflow stream were processed in the old vacuum flash system. The remainder of the overflow stream (2000-2500 lb/hr) was processed in the new vacuum flash system for the purpose of collecting 55 gallon samples of antisolvent deashed SRC. During other periods of Lummus Unit operation the total combined overflow and underflow streams were processed in the old vacuum flash system.

Early in the reporting period increasing difficulty was experienced in maintaining adequate vacuum in Vacuum Flash Drum A. The fusion point of the vacuum bottoms dropped below design and a considerable amount of process solvent was lost in this stream. On July 10 the system was brought down to inspect the two stage steam eductor vacuum system. The gasket between the steam nozzle and nozzle holder on the second stage eductor, which was found to be severely eroded, must have been leaking. A new gasket was fabricated and installed. The water spray nozzle to the second stage intercondenser was partially plugged. After it was cleaned and when the system was tested, the jets produced a vacuum of 29 inches Hg pulling against a blind inserted at the Vacuum Flash Condensate Drum. The system was returned to service on July 11 and specification or higher fusion points were obtained. Nevertheless, toward the end of July the vacuum began to decrease again. On August 1, the vacuum jets were disassembled and the steam nozzle gasket on the secondary jet was found to have been leaking. A new bronze gasket was installed and the old vacuum flash system was returned to service. This gasket was reworked again on August 22. This time, a lead wool seal was installed to reduce leakage around the gasket.

On June 30, an attempt to route the total antisolvent-free underflow from the Lummus Unit directly to Vacuum Flash Drum B was unsuccessful. Previous analyses of this stream had indicated that recovered vacuum bottoms would have a solids content below 40%. After feeding the underflow stream to the flash drum for 35 minutes, however, flow was lost through the flash drum level control valve at the bottom of the downleg. Laboratory analyses later indicated that the vacuum bottoms solids content was about 46%. Previous experience with the Vacuum Flash Systems has indicated marginal operation in this solids range. Fluctuating composition and rate from the settler underflow probably resulted in solids higher than 46%. Piping revisions were made to interchange the function of Vacuum Flash Drums A and B. A slip stream of antisolvent-free overflow can thus be processed in Vacuum Flash Drum B while the balance of the overflow together with the underflow can be processed in Vacuum Flash Drum A. This will also allow processing of slops at the same time because of the higher capacity of Vacuum Flash Drum A. In addition, a surge vessel was included in the process line-up to improve control of flow, heat input, and composition to Vacuum Flash Drum B.

On July 27 a portion of the antisolvent free overflow stream (2,000-2,500 lb/hr) was fed to Vacuum Flash Drum B. This was continued until July 30 when problems were encountered getting flow through LCV-1465. Feed to the drum was stopped and the drum and downleg were flushed, drained, and steamed. On July 31 a high ash coke-like plug was removed from the block valve immediately above LCV-1465. The manway was removed from the flash drum, and the coke trap (an 8" diameter tube perforated with 1/2" diameter holes at the inlet to the drum) was found to be approximately one-third full of large pieces of high ash coke. The radius of curvature of these pieces indicated that they had fallen off the inside wall of the flash drum heater coil. Vacuum Flash Drum B was returned to service August 6 after the system had been cleaned by hydroblasting. It was then utilized to process 1500-2500 lb/hr of the antisolvent-free overflow stream from the Lummus Unit through August 20. Drum samples of the vacuum bottoms produced here were taken when the material was "on-spec". During periods of Vacuum Flash Drum B operation, Vacuum Flash Drum A processed the remainder of the antisolvent-free overflow stream and all of the antisolvent-free underflow stream.

Close monitoring of the corrosion probe rates on the Light Ends Column and the Wash Solvent Column was begun with the feeding of the high chloride Lafayette Mine coal. Of particular concern was the fact that the Lafayette coal chloride content of 0.2-0.3% was significantly higher than the Colonial Mine chloride (0.04-0.07%) and could possibly accelerate attack on the already badly corroded Wash Solvent Column shell and reboiler bundle. During the Lafayette run of July 6 through 15, corrosion rates in the column did increase significantly (greater than 100%). When feed coal was switched to Powhatan

late on July 15 and again on July 20 to Colonial coal, corrosion rates returned to their previous levels. During this period, a Betz neutralizing amine, WS-66, was being injected into the feed line at 150 ppm. Although it is theorized that the increased corrosion is directly related to the high chloride content of the Lafayette coal, all the data has not been completely evaluated to substantiate this. A complete report will be issued at a later date.

On August 26, a special 80-drum sample of process solvent with a 550°F initial boiling point was prepared by reprocessing process solvent. This material was prepared for Texaco, Inc., Montebello, CA for use in gasification tests on SRC-II vacuum bottoms.

During the shutdown the following work was completed or in progress in Area 04:

All 21 trays in the Wash Solvent Column were removed for inspection. These trays were predominately of Hastelloy G, with one test tray each of Incoloy 825 and Hastelloy C. In the upper section of the column, only the Hastelloy C tray had not suffered extensive corrosion attack. The trays in the lower section, however, were in reasonably good condition. Since replacement Hastelloy C trays could not be procured within an acceptable delivery time, it was decided to move the Hastelloy G trays from the bottom section up to the top and to install more easily obtained 316 stainless steel trays in the lower section. The reboiler tube bundle for the Wash Solvent Column was removed for retubing with 316.

Inspection of the Light Ends Column indicated that the lower section of the shell and the 316 stainless steel packing as well as the packing support ring required replacement. Neither the Wash Solvent Column tray replacement nor the Light Ends Column lower section repair had been scheduled for the current shutdown.

Replacement of the top section of the Wash Solvent Column was nearing completion. The 316L stainless steel section was being replaced with a similar section made from 317L. This section of the Wash Solvent Column had already been replaced once; originally it was made of carbon steel. Completion of this work is expected in mid-October.

Early in the period, a section of the carbon steel light ends reboiler bottoms piping from LCV-231 to the inlet of the Wash Solvent Column was replaced with 316L stainless steel. This substitution was part of the pre-shutdown work schedule and this work presented no problem. However, during the shutdown it was determined that the remaining section from LCV-231 back to the Light Ends Column reboiler also required replacement. This section will be replaced

in-kind with carbon steel for the present, but will eventually be replaced with 317L stainless steel. A similar inspection of the Wash Solvent Reboiler bottoms piping also indicated metal loss was occurring, but that replacement was not immediately needed. New piping will, however, be prefabricated for installation in the near future.

Repairs in the vacuum flash system consisted of inspection of both vacuum flash drums, replacement of the inlet stream impingement plate in the Vacuum Flash Drum A, cleaning and inspection of the overhead cooler and installation of a new, larger capacity, spare vacuum flash feed accumulator pump. Piping in this system was also being rerouted to eliminate a troublesome downleg. New vacuum jets for the system will be installed prior to startup.

E. Gas Compression and Naphtha Unit (Area 05)

A faulty lubricator pump was repaired and the machine performed well until July 31 when it developed a severe knock. It was taken off line and new valves and rings were installed. The old valves had a heavy sludge buildup. It was uncertain whether this buildup was process derived or residue deposited from the molybdenum disulphide lubricant still used in this machine.

F. Product Solidification (Area 08)

On August 16, the Sandvik belt along with the limit switch and the limit switch mounting frame were damaged when the limit switch failed to shut down the belt as it tracked too far to one side. Repairs required eleven hours. Additional adjustments were required August 18, 22 and 23 to correct minor tracking problems.

A tentative design package was agreed upon to remove solvent emissions from the Sandvik belt vent stack (whistle tube). Basically the design incorporates a packed bed scrubber using process solvent followed by a high energy John Zink water venturi and cyclone separator, both of which were transferred from waste treatment equipment no longer in service. An electrostatic precipitator may be purchased to collect emissions that pass through the scrubbing system. The problem of siting the electrostatic precipitator was resolved by locating it in an unclassified area. Detailed design began in September.

G. Process Waste Disposal (Area 09.1)

Plans to install a 600,000 gallon storm water collection pond have been suspended because: 1) bids were in excess of design

cost estimates and 2) modifications to the system have resulted in substantially improved performance. Changes which have been made to the system include tighter control of pH in the reactivator to improve flocculation, installation of a centrifuge to remove solids and oil that were previously recycled, installation of an "oil mop" skimmer to remove light oil from the surface of the surge reservoir, and installation of a new oil/water separator at the inlet to the waste treatment area to remove both light and heavy oil from the inlet stream. Work is also underway on the installation of a new Oil/Water Extraction Column. When completed, this column will remove oil from the water stream of the Recycle Process Water Tank.

H. Tank Farm (Area 09.2)

Efforts to recover the oil contained in an oil/water/solids emulsion which had previously been returned to the tank farm were discontinued. The high solids content of this material fouled the steam coils in the recovery tanks, making removal of water impractical. The material was shipped for disposal. This material had originally been pumped from the bottom of the surge reservoir in the waste treatment area.

I. Gas Systems (Area 09.5)

Installation of the new motor control center for this area was completed.

1. Inert Gas Unit

Work on this unit during the period September 11 through September 29 consisted of hydroblasting the MEA exchangers and MEA coolers, sealing the natural gas leaks, overhaul of the nitrogen dryer controls, installation of an additional dryer after-filter, and steaming of the inert gas header and all laterals. A second, finer mesh screen was added below the stripper reflux ceramic packing to reduce the amount of ceramic fines in the reboiler. Tie-ins were made for the future installation of another MEA cooler and filter.

2. Hydrogen Unit

On July 9, the syn-gas compressor was running hot and the drive motor was drawing excessive current. The hydrogen reformer discharge pressure was lowered slightly to reduce the current draw until the compressor was shut down on July 10. Valves, rings, motor, and belts were checked but only the valves had to be replaced. A thicker head gasket was installed to reduce the compression ratio. This change reduced the current demand to normal levels and the compressor performed reliably for the remainder of the reporting period.

Maintenance on this unit consisted of overhaul of the steam and pressure gas controls, hydroblasting of the syn-gas compressor after cooler tubes, screening of the reformer catalyst, and removal of the low temperature shift catalyst. The low temperature shift catalyst will not be replaced because sufficient fresh hydrogen purity is obtainable without it.

J. Dowtherm (Area 09.8)

Two unscheduled shutdowns of the Dowtherm heater were experienced in August, one caused by a power outage and the other by a false high stack temperature. Scheduled shutdown work to improve reliability included an upgrading of the controls, a general overhaul of the fuel gas system and relocation of the heater temperature control to the main control room.

K. Lummus Deashing Project (Area 10)

The Lummus Deashing Unit produced near specification product starting June 25. From June 25 to July 2, settler underflow rates were gradually decreased and antisolvent rate was increased with overflow ash concentration remaining near specification. On July 2, an attempt was made to introduce stripped underflow from the Lummus Unit to Vacuum Flash Drum B so that specification product would be recovered from the overflow stream through Vacuum Flash Drum A. However, because of instabilities in the underflow stream from the settler and the unavailability of a suitable surge vessel upstream of Vacuum Flash Drum B, the feed composition could not be adequately controlled. The attempt to feed both vacuum flash systems was aborted when the downleg of Vacuum Flash Drum B nearly plugged with very high ash vacuum bottoms.

Modifications to the vacuum flash system were underway, but before these modifications could be completed, feed to the Lummus Unit had to be stopped because of indications of a consistently declining rate of recovery of ash from the settler vessel. The settler was purged by recirculation on July 2 and 3 and showed little ash accumulation. On July 4, feed was again introduced to the settler at half the design rates. Full flow to the unit was established July 5 and maintained until July 7, when a leak developed on the antisolvent underflow stripper tower. Slurry impinging on the vessel wall opposite the feed inlet nozzle and control valve (PCV-1743A) had thinned an area one and one-fourth inches in diameter on the wall with a hole approximately 1/16 inches in diameter. Repairs were completed by installing a wear plate and by replacing the thinned section of the vessel. Feed pressure control valve (PCV-1743A) was also inspected and the valve body was badly worn. To protect the body from further erosion a 4-1/2" extended tungsten carbide seat was installed. The existing 1/2" 440 stainless steel Micro-Form trim was replaced with 1/2" tungsten carbide trim.

The unit was ready for feed July 12, but a low process solvent inventory delayed the introduction of feed until July 20. After approximately one hour, leaks developed in the packing of the block valves on the settler pressure relief system and feed was stopped. Feed was introduced to the unit on July 21 at half rate. The rate was increased to 8300 lb/hr on July 22 and was maintained at this level until August 20, when slurry feed to the unit was stopped to prepare the pilot plant for a scheduled shutdown. One 14-hour feed outage was taken on August 4 because of problems with the inert gas blower in Area 01. Prolonged steady state operation was not achieved, due, at least in part, to inter-compartmental leaks which had developed in the settler vessel. During periods of acceptable overflow clarity, samples of specification vacuum bottoms were drummed for storage.

A considerable amount of operating time was required to flush the bottom section of ash accumulations. Adjustments of the feed rates to various settling compartments, adjustments of the antisolvent ratio and adjustments of the overflow to underflow ratio were made. Also, recirculation of both underflow and overflow was utilized in an attempt to clear this section. Eventually it was suspected that a leakage of material between the deashing sections was causing the continual presence of ash in the bottom compartment. This suspicion was verified during a preliminary inspection of the settler during the plant shutdown, as the internal manways on the top and middle trays and the welds on both the middle underflow nozzle reinforcing pads exhibited leakage. Approximately 700 gallons of a coal solids sludge was removed from the antisolvent-free overflow reservoir prior to opening the vessel. When opened, this compartment contained approximately 13 inches of additional sludge. The upper and lower settling trays had deposits of about 2" to 4" thick extending approximately five feet up the trays from the vessel underflow nozzle. The middle settling tray had deposits approximately 1/4" thick which extended about two feet up the trays.

Twice during the reporting period, two Lawrence pumps were shut down due to loosening of the impeller nut which permitted the impeller to wear against the liners and shaft. On June 30, GA 101S, the spare topped feed surge drum circulation pump, was shut down due to reduced output. When inspected, it was found that the impeller vanes had been worn down from abrasion against the liner. On July 28, GA 101, the primary topped feed surge drum circulation pump, was shut down due to high amperage draw, and again the same problem was found. Lawrence was informed of the problem and they are modifying the design of the impeller nut.

III. Pilot Plant Process Analytical Data

Kentucky Nos. 9 and 14 coal from the Colonial Mine was used between June 25 and July 6 and between July 18 and August 21 to prepare

coal slurry for Lummus Unit testing. Kentucky No. 9 coal from the Lafayette Mine was used between July 6 and July 16 to conserve the Colonial Mine coal. Pittsburgh Seam coal from the Powhatan No. 5 Mine was used on July 16, 17, 18 as a replacement for the Lafayette Mine coal which proved to be unsatisfactory for the production of process solvent. Powhatan coal was also used from August 21 to August 25 to process miscellaneous accumulated liquids. The data referred to in this section was obtained during SRC-I operation with either Colonial Mine coal or Lafayette Mine coal. Data obtained during the periods of Powhatan operation has been omitted because it was used only to keep the plant onstream. As the plant was in a turnaround during September, only analyses for Area 09.1, Process Water Treatment, are presented for that month.

The average analyses of selected samples analyzed on a routine basis are shown in Tables A-2 through A-14.

During Lummus Unit testing, a portion of the overflow stream was processed through Vacuum Flash Drum B. The vacuum bottoms thus produced were analyzed separately and gave typical results as shown in Table A-10.

IV. Pilot Plant Special Studies

A. Short Residence Time SRC-II Test

During the period from July 16 through July 18, a brief test run was made in the SRC-II mode using one-half the normal dissolver volume.

Table A-15 lists the primary reaction conditions used during the run. The concentration of solids in the recycle slurry increased during the first 18 hours of the run, requiring additional dilution solvent to maintain smooth operation in the coal blending area. At lineout, the recycle slurry contained approximately 24% solids, resulting in a blend tank solids concentration of approximately 44%. In addition, the relatively low conversion of SRC attained at short residence time conditions resulted in an unusually high (47.1 wt%) concentration of SRC in the recycle stream. Despite the high levels of solids and SRC in the feed slurry, unit operability during the run was reasonably good. Only two brief coal outages occurred during the period, neither of which was attributable to slurry blending problems.

Table A-16 details an estimated product yield structure for the short residence time run. These results indicated increased production of SRC, lower liquid yields, and lower hydrogen consumption at the 0.58 hours dissolver residence time as compared to one hour residence time. These results may be somewhat biased by an insufficient lineout time preceding the run period and by the relatively short duration of the run itself. Should further interest in short residence time SRC-II arise, a complete material balance run could be undertaken with reasonable confidence of successful operation.

B. SRC-I Process Solvent Inventory

Weekly liquid inventory measurements were made throughout the recent SRC-I operating period. The basis of these determinations included measurements of levels and compositional analyses of approximately 30 tanks and process vessels. The data obtained for process solvent and raw solvent inventory are presented in Figure A-1.

The data shown in Curve 1.1 (Figure A-1) indicate a generally negative trend in process solvent inventory throughout the period. Since there was only a small quantity of solvent withdrawn from the process as samples during the period, the decline in process solvent inventory must have resulted from process or mechanical losses during this time. Additionally, nearly 800 barrels of raw solvent were added to plant inventory (the accumulated quantity of raw solvent added is shown as Curve 1.2). Assuming that all of the added raw solvent acted to augment process solvent inventory, the raw solvent contribution to process solvent inventory has been subtracted to produce the net process solvent Curve 1.3.

Curve 1.3 shows that, discounting the make up of raw solvent, a process solvent inventory decline of nearly 1,000 bbl. occurred during the period. In the Lummus Unit operating periods, shown on Figure A-1, there appears to be no clearly discernible acceleration in solvent inventory decline. The solvent loss would seem to be attributable to operation of the plant in the SRC-I mode.

C. Lummus Deashing Unit

The period from June 15 to July 3 is designated as the second Lummus Deashing Unit run. The run terminated when it appeared, from ash balance calculation, that insoluble matter was building up in the settler, as it had during the first run (see second quarterly report, 1979). The unit was purged by recirculating antisolvent-free overflow and seemed to recover satisfactorily, indicating only minor, if any, buildup.

Based on the experience of the first run, the startup procedure had been modified to monitor and prevent an overprecipitated condition. Feed was introduced to all compartments at full design rates and the antisolvent concentration and overflow/underflow split were gradually changed, with constant monitoring of ash balance, in the direction of design condition. The Taylor wedge flowmeters on the six individual underflow lines were removed prior to the run because they were restricting the flows in these lines, thereby increasing chances of plugging. The individual underflows were controlled using the response of the flowmeter on the combined underflow stream when each individual underflow control valve was closed and then opened. Despite these efforts, there were still difficulties in maintaining flow in the underflow lines, especially as the settler

approached design conditions. The alternate opening and closing of the individual underflow control valves may have contributed somewhat to the plugging problems. The considerable instability in flow rate and composition of the underflow streams made evaluation of the unit's performance very difficult.

During the run, the combined antisolvent-free overflow stream displayed ash concentrations low enough to produce specification SRC-I solid product on only a few occasions. However, analysis of individual overflow samples often showed significantly less ash than the combined stream, which suggested that ash was being introduced downstream of the settler vessel. This was attributed to carryover from the underflow stripper whose overheads were introduced, with the overflow stream, to the antisolvent fractionator. However, this was not conclusively demonstrated.

The problem of accumulating gas in the upper settling compartment continued throughout this run. A level control system based on a capacitance type element was installed prior to the run but failed to perform reliably.

On June 30 an attempt was made to route the total flow of underflow stripper bottoms to the Vacuum Flash Drum A, thus allowing the overflow to be processed separately in the Vacuum Flash Drum B. The route taken by the underflow was directly from the underflow stripper bottoms pump to the new Vacuum Flash Preheater inlet.

At this time the settler was operating at near design SRC recovery. After approximately 35 minutes, flow from Vacuum Flash Drum B downleg was lost. Laboratory analysis of the feed indicated that during the period in which underflow had been fed to the flash drum, the solids concentration in the vacuum bottoms had risen to above 45%. Previous experience at Fort Lewis has indicated that, at 45% solids, vacuum bottoms loses the fluidity needed for discharge from a barometric downleg system. It would appear that, if specification SRC-I product is to be produced at Fort Lewis with the Lummus Unit operating at design condition, then a portion of the overflow material will be required for dilution of the underflow to ensure continuous operation of the underflow Vacuum Flash Unit.

The third Deashing Unit run extended for thirty days from July 21 to August 20. During this run the unit was able to demonstrate production of low ash overflow for three periods of 94, 84, and 56 hours respectively. The overflow/underflow ratio during the first two periods was 55/45. In the third period the ratio was raised to 63/37. As in previous runs the most significant control problem was pluggage in the underflow withdrawal lines. The frequency of plugging continued to show a correlation with SRC recovery; i.e. higher SRC recovery usually meant more frequent plugging in the underflows.

Operation was reasonably steady with SRC recovery between 60 and 70 percent. During this run a somewhat different technique was used to control the underflow removal. All six individual settler underflow valves were fully opened and the underflow was controlled by the total underflow flow controller. This mode of operation reduced some of the underflow plugging problems experienced in the two earlier runs when the underflows were controlled individually. Due to fewer plugging problems, the deashing unit operation was more nearly lined out than in the earlier runs. However, the flow rate of the individual underflows could not be controlled or monitored by this mode of operation. By shutting off all of the individual underflows, except the one to be tested, each of the individual underflows was tested for pluggage and/or flushed out every several hours. To what extent the procedure of blocking off five of the individual underflows upset the unit was not known.

Unit ash balances during the third run generally indicated a 10 percent ash loss. This may have resulted from intermittent slugs of high ash material which exited the unit during frequent blowdowns of the underflow streams and which were not usually sampled for the ash balance calculation.

Antisolvent losses for the entire period were not evaluated because of changing operating conditions. However, during a two day period of constant operating conditions near the end of the month an overall unit balance indicated that antisolvent losses were approximately one percent of the antisolvent circulation rate.

Venting of gas accumulation in the settler has continued at a low continuous rate. Gas analyses indicate that the non-condensable gas in the settler and feed surge drum are of similar composition and are mostly hydrogen and nitrogen and condensable vapor vented from the settler was calculated to be consistent with antisolvent losses mentioned above.

D. Rheological Study

A rheological experimental program has been designed to gather viscosity data on SRC-II feed slurry, recycle slurry, and vacuum bottoms over a wide range of conditions. The ultimate goal of the program is the development of a mathematical model of viscosity behavior as a function of the major intensive and extensive variables within the limits of commercial significance.

The primary laboratory tool is a Haake Rotovisco RV-2 viscometer, which was selected following an extensive equipment search for an instrument capable of precision measurements at the elevated temperatures and pressures contemplated for the study.

The selected equipment consists of the following components:
A model RV-2 operating console, drive motor and support stand;

a DMK 50/500 dual range torque head; a D-40/300 viscosity sensor autoclave with constant temperature circulator; a programmer; an X-Y-T recorder; and associated accessory equipment. This system is designed to allow viscosity measurement at pressures to 580 psi and temperatures to 572°F.

When the Rotovisco was first set up in the manufacturer's representative's presence on June 7, several problems were discovered. The external heat exchanger on the heater/circulator arrived improperly mounted, so that heat transfer fluid could not be pumped to the sample vessel. A set of high temperature thermometers was also missing and the cables designed to connect the motor, measuring head, and controller were too short.

The constant temperature circulator was recalled to the factory for repair, and was received back at Fort Lewis on July 12, 1979. The missing thermoregulators were replaced, but with the wrong items, causing further delay in high temperature work. Replacement cables have not yet been supplied, although they have been promised.

While the problems described above were being resolved, exploratory experimental work was begun with the high pressure measuring head. Initial measurements indicated a problem with the magnetic drive unit which introduced severe errors in torque readout at low shear rates (less than 90 per second).

In an effort to diagnose the cause of the fluctuating torque readings, tests were run with various portions of the pressure probe removed. The largest change in output occurred when the bolts securing the autoclave head were removed. These bolts proved to be of carbon steel construction and thus subject to magnetic attraction. The drive spindle housing, drive casing, and drive spindle bearing also might require replacement as each has an effect on torque output.

The German manufacturer of the Haake instrument studied the problem and suggested the following:

- 1) Pressure probe measurements should not be made in the low range (0-50g.cm) of the DMK 50/500 torque measuring head.
Pressure probe operation should be restricted to 0-500 RPM rather than the published 0-1000 RPM range.
- 3) The bolts in the pressure probe autoclave should be replaced with non-magnetic material.

The limitations on shear rate and shear stress imposed by the constraints outlined above restrict the range of permissible measurements as shown on Table A-17. The effect on permissible viscosity measurements is shown in Figure A-2. In spite of the recommended limitations, much of the originally specified range may prove to yield sufficiently accurate data.

Although the experimental schedule has been unavoidably set back due to the Rotovisco equipment problems, the operable components have been used with a direct drive ambient pressure probe to test simple samples. To temporarily replace the heater/circulator, an electric drill pump has been used to circulate water through the sample tempering vessel. Steam has also been circulated through the sample cylinder. Using this setup, viscosity measurements have been satisfactorily made at atmospheric pressure at temperatures to 220°F. Although both temperature and pressure were too low to make the data of immediate utility in process scale-up, the experiments indicated the sensitivity of slurry viscosity to solids concentration, temperature, and composition.

For artificial slurries made from SRC-I dried mineral residue and process solvent at 57°F, added solids had a stronger effect on viscosity than either the Kunitz equation,

$$\frac{\mu_m}{\mu_l} = \frac{1 + 0.5 \phi_s}{(1 - \phi_s)^4}$$

or the relation of Mori and Ototake²,

$$\frac{\mu_m}{\mu_l} = 1 + \frac{1.56 \phi_s}{0.52 - \phi_s}$$

would predict. This is shown in a comparison of actual and predicted viscosities on Table A4. (In the preceding equations, μ_m is the mixture viscosity, μ_l is the viscosity of the liquid alone, and ϕ_s is the volume fraction of solids.) Figure A-3 compares the relative viscosity (μ_m/μ_l) versus volume fraction of solids for both the experimentally measured data and that predicted by the above relations.

Both the Kunitz and Mori and Ototake equations are considered most accurate for $\phi_s \leq 0.1$. However, Mooney's correlation³

$$\ln \frac{\mu_m}{\mu_l} = \frac{2.5 \phi}{1 - C \phi_s}$$

is sometimes applicable to ϕ_s as large as 0.5. The coefficient C evaluated from data usually varies from 1 to 1.5 for monodisperse systems. For the artificial SRC slurry, C fluctuated but was usually above that range (see Table A-18).

Atmospheric pressure viscosity measurements were also made on an SRC-II recycle slurry sample using a steam heating jacket to control the sample temperature. The results showed large

1. Chemical Engineers' Handbook, 5th Edition, Perry and Chilton, Ed. Page 3-247.
2. Ibid, page 3-247.

variations in viscosity for small temperature variations. The sample, which was solid at room temperature, had the following measured viscosities:

$T(^{\circ}\text{F})$	μ (cp)
221.0	5300
218.5	5850

Such viscosity variation with temperature is at a rate of approximately 3.8 percent per degree Fahrenheit, approximately the normal rate for most organic liquids.

The demonstrated strong effect of temperature on viscosity is supported in theory by the de Guzman-Andrade equation, $\mu = Ae^{B/T}$ which is the basis for correlating viscosity to temperature (where A and B are constants evaluated by correlation). The sensitivity of viscosity to temperature can be seen in the derivative:

$$\begin{aligned} \frac{d\mu}{dT} &= \frac{-ABe^{B/T}}{T^2} \\ &= -(B/T^2) \mu \end{aligned}$$

The magnitude of the temperature effect is proportional to the viscosity, μ , so that thicker material, such as recycle slurry at atmospheric saturated steam temperature, is extremely sensitive. The same material at higher temperature should be much less sensitive to temperature change. Nevertheless it is apparent that all experimental viscosity measurements with coal solution will require very precise temperature control and measurement.

Examination of previously measured viscosity data has suggested inherent problems in proper characterization of coal-derived materials. Data for two recycle slurry samples from the recent Powhatan half-dissolver run show a large variation in viscosity measured on a Brookfield viscometer, yet only small apparent variations in composition. The composition and viscosity data for two samples taken on May 27 and May 29, 1979 are compared in Table A-19. Pyridine insolubles and ash percentages each change less than one percent from sample to sample. Heavy distillate and vacuum bottoms make up most of the sample (98.99% by vacuum distillation for sample 113101 and 99.10% for sample 113124). Both heavy distillate and vacuum bottoms concentration have relative changes of less than two percent. However, the viscosity drops 31.25% and 20.49% from the first to second sample at temperatures of 295 and 305°F, respectively.

3. Ibid, page 3-247.

Temperature measurement inaccuracy could account for a small part of the viscosity difference. However, a temperature bias of approximately 9°F between the series of viscosity measurements of each sample is needed to totally account for the viscosity change. Torque readings and subsequent conversion to shear stresses could also be inaccurate and account for the difference in results. Another possible explanation is that the samples were analyzed too coarsely to detect compositional variations that significantly effect viscosity. The "Vacuum Bottoms" cut, which is over 80% of the samples, may differ significantly in composition from sample to sample. The first sample may contain polymeric material with higher average molecular weight than the second sample. The higher end point temperature of the first sample does indicate higher average molecular weight and could explain the higher viscosity.

Use of the Haake viscometer should reduce doubt as to temperature and shear stress readings. Still, viscosity correlated to composition based on the current standard laboratory characterization and analysis will have inherent error. A more refined analysis may be required to allow characterization based on finer "cuts" of the amorphous sample material.

After the remaining parts necessary for high temperature viscosity measurements with the Haake system were received, tests of the circulator system demonstrated a capability of very precise temperature maintenance ($\pm 1/4^{\circ}\text{C}$) within the published range.

To date the Haake Rotovisco manufacturer has supplied only a replacement set of non-magnetic bolts. Tests run with the new bolts show a continued presence of signal noise, particularly at low shear rates. The magnetic drive also appears to add approximately ten percent to viscosity measurements made with a direct drive probe.

At the suggestion of the German Haake viscometer manufacturer, two separate torque measuring heads were obtained replacing the dual head originally furnished with the apparatus. Torque measurements made with the new head, nevertheless, indicated a continuing substantial bias in viscosity measurements made with the magnetic drive probe.

In an effort to correct the data obtained with the magnetic drive probe, a series of calibration runs was made. In these runs, torque was measured as a function of shear rate with no sample in the magnetic drive probe. This data, shown on Figure A-4, indicated a significant offset in torque reading due probably to bearing friction. This error appeared to be repeatable, however, so that a correction curve could be used to correct measured torque to a zero drag value for most of the torque range. However, the data measured with the expanded low torque scale (shown as the inset to Figure A-4) showed the limitations of this procedure in extending it to the low shear

range. Data taken below approximately 150 sec^{-1} showed an unexpected inflection and any simple, constant or proportional correction factor would break down.

Torque measurements were made on a commercial viscosity standard using the direct drive sensor and these data were compared to data for the same sample on the magnetic drive probe with the offset subtracted. This comparison tested the effectiveness of the offset in torque reading as a correction for bias in the magnetic drive probe. Again, torque was measured as function of shear rate. After subtracting the offset from data measured with samples using the high torque range MK500, the direct drive viscosity standard data was reproduced closely as seen in Figure A-5.

The same comparison in the expanded low torque MK50 scale (shown as the inset in Figure A-5) showed differences that make such a correction ineffective below approximately 150 sec^{-1} and only useful to within 20 percent over the remaining useful range of the MK50.

The correction procedure developed will be used for future measurements using the magnetic drive. The procedure will be rechecked periodically to detect possible change of the correction.

E. Vacuum Flash Test Stand

Piping, instrumentation and structural drawings of the vacuum flash test stand were completed. The structural support framework for the test stand was installed and control panel outfitting was nearly complete. The preheater was installed but retrofitting is still required. Both the vacuum bottoms and the condensate receivers were fabricated. Further construction will continue after annual turnaround modifications have been completed.

When the test stand is completed, a short series of tests will be conducted with a full-range petroleum derived oil to establish operability. Standardization tests will then be conducted at a flash zone temperature of 740°F at absolute pressures of 50, 30, and 10 mm Hg, respectively.

Following drum calibration runs, SRC-II recycle slurry will be fed to the unit to study vapor-liquid equilibrium and solids carryover to the condensate stream. For the vapor-liquid equilibrium study, a three level factorial experiment in temperature and pressure is planned and outlined below.

<u>Feed Temperature</u>	<u>Absolute Pressure</u>
700°F	30, 20, 10 mm Hg
750°F	30, 20, 10 mm Hg
800°F	30, 20, 10 mm Hg

During each of these runs, samples of feed, vacuum bottoms and condensate will be analyzed to obtain the following information:

Feed

- 1) Cushman Distillation
- 2) Ash
- 3) Pyridine Insolubles

Vacuum Bottoms

- 1) Ash
- 2) Pyridine Insolubles
- 3) Melt Point
- 4) Viscosity at 550°F

Condensate

- 1) Cushman Distillation
- 2) Ash
- 3) Dissolved Gas

A wet test meter will be used to measure the volumetric flowrate of non-condensable material and samples of the vapor will be analyzed by gas chromatography.

Subsequently, the vacuum flash test stand will be used to study the effects of vapor velocity, drum geometry and drum internals on the mechanical carryover of solids into the condensate stream. Vapor velocity will be varied by changing feed rate to alter vapor loading in a given drum and by installing vessels of varying aspect ratio. At present, drum diameters of 8" and 3" are planned, which will allow variation of vapor velocity from 2-35 ft/sec. Drum internals will be varied by installing feed distributors and/or demister mats in the test vessels. Although no firm plans for varying drum geometry presently have been made, asymmetrical drums are being considered to study slurry entrance and vapor exit effects.

Consideration is also being given to the possibility of conducting further tests to determine the maximum flash drum temperature and the efficiency of steam stripping. Plans for these experiments, however, are incomplete at this time.

F. Dissolver Mixing Study

From June 27 through June 30, radioactive argon-41, bromine-82 and gold-198 were each injected separately upstream of the preheater to determine the degree of backmixing in these units. The degree of backmixing was calculated by measuring the delay time between the time of injection and the time 67% of the material had exited the system.

As shown in Table A-20, the transit time through the preheater was longest for the flake gold particles (10-40 micron), intermediate for the colloidal gold and bromophenanthrene (Br-82) and shortest for argon-41. The delay time for argon was short (narrow peaks) indicating that little backmixing occurs in the preheater. Conversely, the delay time from bromophenanthrene was very long indicating that for the liquid phase a high degree of backmixing occurs. No conclusions can be made concerning the transport of solids through the preheater since the detector responses were so small.

Since part of the bromine, most of the colloidal gold and nearly all of the flake gold were retained in the preheater, these tests will be repeated to obtain more complete data on the dissolver using a new injection point just upstream of the dissolver. The new injection point was installed during the shutdown.

G. Lawrence Pump Performance

1. Description of the Lawrence Pump

a. General

The pump, which meets the requirements of API 610, is a partially lined, 3" x 1 1/2" - 15" horizontal pump with a radial split case. The pump is designed for end suction and top discharge with the casing and bearing frame centerline supported (the casing is mounted on water cooled pedestals).

b. Casing

The casing is designed for operating pressures up to 300 psig with 300 lb ANSI inlet and outlet flanged connections. The casing is split radially to permit removal of the rotating elements without disassembling the suction and discharge piping. The casing base metal is 410 stainless steel to which is applied an abrasion resistant coating. The 410 stainless steel casing has a hardness of approximately 350-400 Brinell (BHN) before coating. Coatings of "Com-o-Lox" ceramic and LPI-5 (Lawrence Pump proprietary) have been used with the LPI-5 coating giving somewhat better performance.

c. Liners

ABEX Cor. HC250 liners (BHN-550) are provided for the suction disc and the hub disc. The suction disc liner extends out to the face of the inlet flange.

d. Impeller

Maximum diameter is 15 inches. The impeller is made of HC 250 with BHN of 550. The impeller is a tapered, enclosed design with repelling vanes on both the front and back shrouds.

e. Mechanical Seal

John Crane 15W bellows seals have been installed through most of the service life of the pumps.

2. Performance History

a. General

There are a total of 6 Lawrence slurry pumps described above in service at Ft. Lewis. Five of these pumps are installed in the Lummus Deashing System and were in service while that system was in operation. The sixth pump is in service on the Filter Feed Surge Vessel (FFSV). The FFSV is used as a holding tank for various waste streams awaiting processing through the Vacuum Flash Drum for recovery of process solvent. The pumpage varies in consistency but in general has less than 10% solids and a viscosity of less than 100 centipoise. The pump takes suction from the bottom of the FFSV and can either send the pumpage forward to other parts of the plant, or recirculate through a heat exchanger to the FFSV for heat up or to boil off water. Approximately 95% of service time of the pump has been in the recirculation mode.

During the Aug-Sept 1979 plant shutdown one of the Lawrence pumps from the Lummus Unit was moved to the Area 01 slurry circulation loop for evaluation and to improve operability of that system.

b. Overall reliability of these pumps in slurry service has been poor to date. The following is a summary of some major problems.

(1) Mechanical seals - The 5 pumps installed in the Lummus Deashing Unit and the FFSV pump did not run enough hours to adequately test seals. In general, however, seal life has been from 2000-4000 hours in slurry service. This is not a fault of the pump, but nevertheless, seal service life needs improvement. Hour meters have been installed on several pumps so that more specific data can be obtained on seal performance.

- (2) Impeller - Every Lawrence pump in service at Fort Lewis has had at least one occurrence of the impeller nut loosening which allows the impeller to wobble on the shaft. This movement allows the impeller to rub against the hub disc liner and suction disc liner. Lawrence has redesigned the impeller nut and shaft sleeve to try to eliminate the problem. Another possible source of this problem is failure to set the proper clearance between the suction disc and impeller. This would cause the impeller to rub against the suction disc when thermal expansion of the shaft occurs during startup. The heat built up by this rubbing could cause distortion and loosening of the unit. Although the impeller nut was a weak portion of the pump design, it is difficult to draw a definite conclusion as to the actual cause and effect sequence of this failure because there are so many variables. It is felt that this problem will be eliminated with proper assembly techniques and the new nut design.

After 2200 hours of service there was very little hydraulic wear evident on the FFSV pump. There was, however, some wear on the edge of the vanes at the impeller inlet, but not enough to affect performance. It appears that the HC-250 stands up very well to hydraulic wear in this application.

None of the impellers on the other five pumps accrued appreciable service time because of mechanical damage to the impeller; thus no conclusions could be drawn regarding hydraulic wear.

- (3) Casing - All of the pumps have 410 stainless steel casing coated with a hard material for wear resistance. Initially the coating was a "Com-o-Lox" ceramic coating. This coating proved to be unsatisfactory with a service life of less than 1000 hours. An LPI-5 diffusion coating (Lawrence Pump proprietary) was used for the casing installed in the FFSV pump and after 1375 hours the coating was still intact except at the cut water where the coating was gone and the base metal was being eroded. This casing has been returned to service and operation will continue until failure, to determine maximum service life.

Ultrasonic thickness measurements have been made on the pump casing while the pump is in

service. The results to date have been questionable because a satisfactory high temperature ultrasonic probe has not been available. New high temperature probes have been ordered and these measurements will be continued. An accurate casing thickness measurement would allow an estimation of service life without running to failure.

Some conclusions drawn from the initial experiences with these pump casings are (1) the inner wall of the casing should not be broached for bleed and drain connections since accelerated wear occurs in these areas, (2) ceramic coatings are completely unsatisfactory. Diffusion coatings are better but will only provide an estimated 3000-4000 hours casing service life, (3) failure of the casing will probably occur at the cut water, and (4) slurry pumps should have a replaceable casing liner made of HC-250 or similar material to improve service life and reduce replacement cost.

- (4) Disc Liners - The hub disc and suction disc liners showed negligible hydraulic wear. The extension of the suction disc liner out to the face of the inlet flange appears to have eliminated the wear problem that occurred in this area on ANSI pumps used in slurry service.

3. Future Plans

One of the Lawrence pumps from the Lummus Unit has been installed in the Area 01 slurry circulation line. Operation of this pump will be monitored closely. The FFSV pump will be evaluated further to determine ultimate casing life. Two fully lined Lawrence pumps (liners on suction disc, hub disc, and volute) have been ordered with a delivery date of Feb. 1980. One will be installed in the Area 01 slurry circulation loop, but a location for installation of the second pump has not been decided at this time.

H. Pressure Control Valve Performance

There are two stages of pressure letdown in the reaction area. The first stage (LCV-166) occurs between the High Pressure Flash and the Intermediate Pressure Flash Drums. The pressure drop in this service is between 600 and 1400 psi (average 1100 psi). The second stage letdown (LCV-175) occurs between the Intermediate Pressure Flash and either the Slurry Recycle Stripper or the Filter Feed Flash Vessel. The pressure drop in this service is between 400 and 900 psi with an average of 700 psi.

Three different valves have been installed for pressure letdown. Two of the valves were angle valves (1" Fisher DBAQ and a 1" Willis M1-HT) and the third a globe valve (1" Fisher DBQ). The globe valve is no longer in service due to the unsatisfactory performance of both the valve body and the valve trim. After 4 days of service both the tungsten carbide trim and the valve body would show signs of significant erosion.

There are two parallel control valves in each letdown service for a total of four valves. The two valves in the first stage of letdown are a 1" Fisher DBAQ (LCV-166A) and a 1" Willis M1-HT (LCV-166B). Both valves in the second stage of letdown are 1" Fisher DBAQ's (LCV-175A&B).

The time between maintenance of the letdown valves in the reaction area has improved from 4 days in early plant operation to a maximum of over 100 days¹ in the present plant operation. The main variables that affect valve life are:

1. Valve design.
2. Trim materials.
3. Valve sizing.
4. Pressure drop.

The most significant variable in valve life is that of trim material. For example, the performance of tungsten carbide (Kennametal K-602) is at least 100 times better than that of Stellite. However, it is not sufficient for the trim material to be tungsten carbide since there is considerable variation of trim life within the various grades of tungsten carbide. A standard grade of tungsten carbide (6% cobalt binder) has a life of approximately half of that of K-602 (less than 1-1/2% cobalt binder).

In addition to the K-602 and standard tungsten carbide, K-701, K-703 and Valenite 134 have also been tested. The K-701, K-703 and Valenite 134 all appear to perform about equal to the K-602, but because of varying process conditions this has been impossible to quantitatively evaluate. However, the recent addition of the necessary electrical equipment and computer programs to monitor the flow rate, pressure drop and valve position (Figures A-6 and A-7), should enable the ranking of the materials. For example, a relative erosion rate can be obtained from the slope of the valve position versus time plot.

Given approximately equal operating conditions, as in the case of the first stage of pressure letdown (LCV-166), the Fisher DBAQ outperforms the Willis valve (M1-HT) by at least a factor of three and probably closer to a factor of

1. Trim changes before valve lost control (failure)

eight. For example, the DBAQ valve with K-602 trim will normally operate a minimum of 6 weeks even when the tip of the plug (Figure A-7) is broken, whereas the trim life of the M1-HT is a maximum of 3¹⁶ days². The DBAQ valve would probably operate 120 days³ with a K-602 trim if the tip of the plug did not break.

The difference in trim life between the DBAQ and the M1-HT is probably due to the difference in the impingement angle between the two valves. As shown in Figure A-7, the slurry contacts the DBAQ trim at relatively low impingement angles, whereas the impingement angle in the M1-HT (Figure A-8) is approximately 90°. The effect of impingement angle can also be seen by a comparison of the erosion rates between the trim and the bean in the M1-HT. Since the pressure drop across the trim and fixed orifice are approximately equal (estimated at 60% and 40%⁴ respectively for 1/8 inch trim) one would expect the wear to be equal. However, after six trim changes (approximately 112 days) the original Valenite 134 fixed orifice (bean) had shown very little wear. The original fixed orifice is still installed.

One advantage that the M1-HT has over the DBAQ is that the design of the trim results in less breakage. Erosion resistant materials such as K-602, K-701, and K-703 are brittle (low transverse rupture and impact strengths). The M1-HT trim can be fabricated with the erosion resistant trim material in compression. Since tungsten carbide and other brittle materials are strong in compression and weak in tension, this configuration has significant advantages. Conversely, from examination of Figure A-7, the trim in the DBAQ cannot be fabricated with 100% of the tungsten carbide in compression; the tip of the inner valve will always be vulnerable to tensile stresses. However, the susceptibility of the DBAQ trim to breakage will decrease as the cross sectional area of the trim increases (larger trim). Presently, 1/4" trim is being utilized in the DBAQ and trim breakage is reasonably high. In the past, when 1/2" (4 times the cross sectional area) trim was utilized there was very little trim breakage, but the integrated life was shorter than that of a broken 1/4" trim since the valve was markedly oversized.

It is important that the letdown valves be sized correctly in order to achieve maximum trim life. For example, an oversized valve that is only open 10% under normal operating conditions has an erosion allowance of 10% before the valve can no longer maintain control, whereas a correctly sized

2. Valve trim taken to failure.
3. A 100 day live has been achieved; however, the trim was changed before failure.
4. For 42 days of operation the ratio was approximately 20% and 80%, respectively.

valve (assuming 50% open) has over 5 times the erosion allowance.

One method of extending trim life is by utilizing a fixed orifice downstream of the control valve. The advantages to installing a fixed orifice include:

1. Less pressure differential across the trim.
2. Less downstream erosion (M1-HT only).
3. Larger trim size (DBAQ only).

The one disadvantage in both the M1-HT and DBAQ is that a fixed orifice adversely affects the control characteristic of the valves. The performance of the M1-HT was improved by over a factor of three when the pressure drop across the fixed orifice was increased from 40% to approximately 80%. However, the control characteristic of the valve was so adversely affected that the valve barely maintained control. Figure A-9 shows both the flow rate and pressure drop for the M1-HT valve were approximately constant during the time period of 7/20/79 to 8/2/79. However, the valve position was not constant. During this same time period the downstream DBAQ (LCV-175A) valve, which does not have a fixed orifice, maintained an approximately constant valve position. The addition of a restriction orifice adversely affects control ability and could not be applied to vessels with short residence time. That is, the addition of a fixed orifice improves trim life at the expense of pressure vessel size.

The design of the M1-HT mandates a fixed orifice to prevent downstream erosion. When the valve is partially open, the discharge from the trim has a tendency to swirl and cause downstream erosion. The addition of a fixed orifice reduces the swirling effect and therefore reduces downstream erosion.

Since the residence time in the flash drums is relatively large, the overall performance of the DBAQ valves (LCV-166A, LCV-175 A&B) need not be very responsive and could be improved by the addition of fixed orifices. The fixed orifice would improve performance by decreasing the erosion and breakage of the trim in the DBAQ valves. The breakage would be reduced because larger trim sizes would be allowed.

I. Outside Studies

Several programs related to SRC-II have been completed by various agencies and their reports are included as appendixes to this report. The "Chemical Analysis and Leaching of Coal Conversion Solid Wastes" was studied at the Illinois State Geological Survey and can be found in Appendix C. "Mössbauer Spectroscopic Studies of the Mineralogical Changes in Coal as a Function of Cleaning, Pyrolysis, Combustion and Coal Conversion Processes" and "Identification of Potential Pollutants from Coal Conversion Wastes" are included as Appendixes D and E, respectively.

V. Harmarville Process Development Unit P-99

A. SRC-II Operation on Process Development Unit P-99

Process Development Unit P-99 shut down on June 25 for the scheduled summer turn-around. Examination of the unit at this time showed it to be in generally good condition. Comments on specific items are as follows:

Dissolver. Approximately 4 inches of solids were found in the bottom. There was a 1/2 inch thick ring of flaky solids about 2-1/2 feet from the bottom, and a 1 inch thick ring of solids at the outlet; the outlet port was partially restricted. It is estimated that these solids occupied less than 3% of the reactor volume.

High Pressure Separators. All four of the high pressure separators were in good shape. The stainless steel demister pad in the first intermediate separator had disintegrated.

Let-down Valve System. A small amount of erosion was observed in two of the valves and some of the tubing.

Kerosene Scrubber. The stainless steel packing had partially dissolved. Inconel packing was installed.

Vacuum Column. When cut open, the vacuum column was found to be in relatively good shape. The walls of the vessel were coated with about 1/4 inch of tar and coke. The cone-shaped bottom of the column was almost clean, and the outlet line was open. The demister pad was coated with a fairly heavy layer of deposits. Although it is not known for certain, an examination of vacuum column pressure measurements indicates that the plugging of the demister pad may have occurred over a relatively short period of time. The Calrod heater on the bottom cone was found to be burned out. Also, one of the Calrod heaters on the vacuum column preheater had burned out.

Most of the unit modifications made to P-99 during the summer shutdown involved the separator system. Piping changes were made to permit more accurate measurement of liquid flow rates, more accurate temperature control, and improved flexibility for wash water injection.

Some problems were encountered in restarting the unit after the summer shutdown. Shortly after coal feed was restarted, a leak developed in the oil drawoff line from the first intermediate separator. To repair this leak required flushing, cooling, and depressuring the unit. Coal feed was restarted on August 28, but a few days later accidental leakage of an excessive amount of pump seal oil (a highly refined petroleum oil) into Tank 1 caused solids to precipitate in the feed mix tank and plugged the recirculating pumps. While the

tank was being opened and cleaned, solvent was circulated through the unit using the flush pump. There was a recurrence two days later when seal oil again leaked into the mix tank; however, on this occasion it was possible to recover by merely flushing the feed tank. Coal feed was successfully restarted on September 2.

At the occurrence of the first feed tank problem discussed above, it was thought that the coal being used might have been a contributing factor. Therefore, while the feed tank was being cleaned, the coal hopper was emptied and then loaded with coal from a new (fourth) shipment of coal from the Powhatan No. 5 Mine. Inspections for this coal are given in Table B-1.

During September, two runs (Runs 56 and 57) were completed. Run 56 was made at essentially the same conditions as Run 48, except that the average dissolver temperature was lower (851°F), and fractionation temperatures were slightly higher. Run 57 differed from Run 56 only in that dissolver pressure was increased to 2500 psig. Operating conditions for these runs are given in Table B-2 and yields are presented in Table B-3.

Part way through Run 56, a severe leak developed in the Cooper-Penjax recycle compressor, and before the spare compressor could be cut in, unit pressure dropped to 300 psi. This completely upset the unit, and two days' operation was required to re-establish steady-state conditions. The unit then ran smoothly, and three more yield periods were obtained before switching to Run 57 conditions. Later analysis of the data revealed, however, that distillate yields for the three periods after the upset were significantly higher, and bottom yields were significantly lower, than for the periods before the upset. Furthermore, elemental balances for the periods after the upset are not consistent with data from other runs on the same batch of coal. The reason for the change in yields discussed above is not known, but since the periods before the upset appear to be more consistent with the data from other runs, only the early periods were averaged to produce the Run 56 yield structure shown in Table B-3.

Run 57 was ended sooner than desired because of a severe leak in the emergency shut-off valve located in the slurry line between the hot high pressure separator and the pressure let-down valves. Nevertheless, the average yield data for Run 57 look consistent with the rest of the data and are believed to be accurate.

A comparison of Runs 56 and 57 shows that increasing the pressure from 2000 to 2500 psig increased C₅-900°F distillate yield 4-5% and decreased 900°F+ product yield a corresponding amount. Hydrogen consumption and C₁-C₄ gas yield were both about 0.5% higher for the higher pressure operation, while inorganic product yields were about the same.

B. Hydrotreating of SRC-II Naphtha

The naphtha hydrotreating work described in the following paragraphs was not performed as a part of Contract DEAC-0179-ET10104, but rather was funded by Gulf. Summary results of the work are presented in this report because the naphtha was produced with DOE funding on Process Development Unit P-99.

Approximately 300 gallons of SRC-II naphtha produced from Powhatan No. 5 Mine coal were distilled to produce five fractions. These fractions were then blended to produce hydrotreating feeds having distillation cut points of 300, 350, 375, and 400°F, with the initial boiling point of each feed being 150°F. Inspections for these feeds are shown in Table B-4.

The initial part of the hydrotreating work consisted of a variable study. Based on the results of this initial work, conditions were chosen for each feed stock, and production runs were made to produce feed for later reforming work. The catalyst used in the hydrotreating work was very similar to those typically used in hydrotreating petroleum stocks. The ranges of the variables studied during the initial work were:

Pressure	150-1500 psia
LHSV	1-2
Temperature	680-730°F
Gas circulation rate	2500-4000 SCF/Bbl (85% H ₂ purity)

Based on an analysis of the initial work, conditions were picked for production runs to make hydrotreated naphtha for future reforming studies. The products from the runs contained less than 0.2 ppm nitrogen and less than 0.5 ppm sulfur.

C. Vacuum Column Operation

During the third quarter, a series of test runs was made on the vacuum column on P-99. The purpose of this work was to determine the effect of flash zone temperature on the amount of 900°F distillate remaining in the vacuum column bottoms. This was the first systematic study of the vacuum column; and, because of incomplete understanding of all the factors affecting column operation and some equipment problems, the results show considerable scatter. Therefore, care must be exercised in using the data quantitatively. Nevertheless, the qualitative trends appear correct. Because the information learned from this study will prove useful in later work and because the experimental techniques used in future studies will be similar, the vacuum column study is being reported here in some detail.

1. Description of Vacuum Column

The flash distillation that occurs in the vacuum column separates the feed into a distillate overhead product and a slurry bottoms product containing ash and undissolved coal (pyridine insolubles).

The U-shaped preheater carries the slurry from the recycle splitter to the vacuum tower. Preheater effluent is directed against an impingement cone. Vapor leaves the top of the column and slurry drains into a holdup tank. On an hourly basis, a computer controlled valve located between the column and this tank closes. The tank is then manually pressurized with nitrogen and drained. After draining, it is evacuated, and the valve between it and the column is reopened. Figure B-1 is a diagram of the vacuum column.

The feed rate to the vacuum column is erratic due to the oscillatory operation of the pressure letdown valves and the splitter. The letdown valves are not throttling valves, but are off-on valves which function in an oscillating mode. Thus, they send a pulsating stream to the atmospheric flash tower. Another source of pulsations is provided by the recycle splitter, which alternately directs the atmospheric flash column bottoms to the recycle mix tank or the vacuum column on a timed cycle. The combination of these two effects results in the slugging of material into the vacuum column. In order to prevent plugging and coking of the preheater during periods of low feed rate, part of the vacuum overhead product is recycled to the vacuum column feed side of the recycle splitter. This not only assures continuous flow throughout the preheater but also decreases the viscosity of this stream.

2. Procedure

In general, vacuum column flash zone temperature was raised once a day. Then, after approximately 24 hours of operation, the column was sampled, after which flash zone temperature was again increased. Viscosity measurements were usually performed on the day of sampling before the samples were sent to the Analytical Technology Department for further analyses. Sufficient sample was saved to duplicate the viscosity tests and Cushman distillations. Viscosity trials on the same samples after a lapse of a few weeks produced similar results.

a. Run Conditions

The vacuum column testing reported here was carried out during Runs 54 and 55. Operating conditions for these runs are reported in the Second Quarter 1979

Progress Report. For Run 54, the feed rate to the vacuum column (not including the recycled distillate) was 12-15 kg/hr containing 28-33% distillate. The mass flow rate of the bottoms product was 8.5-10 kg/hr, while the net overhead product was produced at a rate of 3.3-5.1 kg/hr.

Run 55 experienced an overall lower vacuum column feed rate, the rate being 10-12.5 kg/hr containing 23-28% distillate. The distribution between the bottoms and net overhead products was 7.4-9.3 kg/hr and 2.7-3.5 kg/hr, respectively.

Feed and product stream rates and compositions and flash zone temperatures for individual periods are given in Table B-5.

b. Viscosity Measurements

A Brookfield laboratory model LVT viscometer was utilized to measure the viscosities of vacuum column bottoms and atmospheric flash column bottoms samples. A Brookfield Thermosel unit, in conjunction with their Model 63A Proportional Temperature Controller, was used to maintain a constant sample temperature. Due to the high viscosities and high melting points of these samples, they were prepared at room temperature in solid form. The finely ground samples were melted in the Thermosel unit prior to the viscosity measurements. For the tests, spindle #34 was connected to the viscometer which was run at eight different shear rates in decreasing order from 16.8 to 0.084 sec^{-1} . Each sample was tested at various temperatures, usually extending over a 100°F range, and the temperature was raised by 25°F increments. The temperature range used for the vacuum bottoms samples was 475-575°F. Results of viscosity measurements on vacuum column bottoms are presented in Tables B-6 through B-10, and results for atmospheric flash column bottoms are given in Table B-11.

c. Product Analyses

In addition to viscosities and distillations, a number of other analyses were obtained on various product streams. Vacuum tower bottoms were submitted for specific gravity, melting point, pyridine insolubles, ash, and carbon, hydrogen, nitrogen, sulfur, and oxygen contents (see Table B-12). Fractionator bottoms and vacuum column overheads (in P-99, these two streams are combined to produce the process solvent product) were submitted for spectrographic analyses to determine trace metals contents (see Tables B-13 and B-14).

3. Data Evaluation

Some operating problems were encountered during the course of this study which may be responsible for some of the scatter in the data. Unit upsets occurred during several run periods, and this may have affected vacuum column operation. Specifically, for Run 54, severe upsets arose during Periods 54-3 and 54-11. During Period 54-3, problems with the amine scrubber caused coal to be out for eight hours, and the tower temperature and vacuum were decreased substantially during this time. After coal feed was resumed, the recycle splitter was temporarily raised 20%, while the temperatures were being brought back to normal. For Period 54-11 problems with the feed pump and Tank 1 viscosity were sufficient to cause unreliable results.

Run 55 also had several upsets. The coal belt malfunctioned an hour before sampling Period 55-1. Period 55-2 experienced a coal outage due to an apparent restriction in the preheater or transfer line, and the vacuum overhead product was not mixed into the process solvent for a time due to the valve in the discharge line to Tanks 8 and 9 being inadvertently closed. Coal was out again in Periods 55-4 and 55-5A. For Period 55-4, this resulted from blown discs on the feed pump, while Period 55-5A experienced problems with flash tower level control which forced the temporary bypassing of the fractionation columns.

Another problem is that there is some variation in the flash zone temperature, probably due to the somewhat erratic feed rate discussed previously. Thus, reported flash zone temperature should be considered as only approximate values. Also, the low values of distillate in the vacuum bottoms led to some difficulty in getting good reproducibility of these data. Average values from repeat analyses were used in data analyses.

4. Results and Discussion

Rheologically, the vacuum column bottoms behaved as a non-Newtonian pseudoplastic, that is, the viscosity decreased with increasing shear rate, but the rate of this decrease was greater at low shear rates than at high shear rates. At a given shear rate, viscosity decreases with temperature as shown by the data in Tables B-6 through B-10, which demonstrates typical pseudoplastic behavior. Figure B-2 shows a linear dependence of viscosity (at constant shear rate) with the reciprocal of absolute temperature.

a. Viscosity and Distillate Recovery

Figure B-3 is a plot of vacuum tower bottom viscosity vs flash zone temperature. In spite of some scatter, the figure shows a clear trend of increasing bottoms viscosity with increasing flash zone temperature. Figure B-4 is a plot of 900°F-distillate remaining in the vacuum column bottoms vs flash zone temperature. In spite of the scatter, a definite trend of decreasing distillate concentration with increasing flash zone temperature is apparent. Since vacuum column bottoms viscosity and distillate yield are both correlated with flash zone temperature, it is not surprising that they are also correlated with each other, as shown in Figure B-5. There appears to be a trend of increasing ash and pyridine insolubles in the vacuum bottoms as flash zone temperature increases.

Limited viscosity tests were conducted on the flash tower bottoms, which was the feed to the vacuum column. Like the vacuum bottoms, the flash tower bottoms conformed to non-Newtonian pseudo-plastic behavior, but was considerably less viscous than the vacuum bottoms. Samples from Periods 55-5 to 55-7 were tested. Viscosities of the vacuum overhead samples were measured by the Analytical Technology Department with results on the order of 5 to 10 cP.

Emission spectrographic analyses of the fractionator bottoms and the vacuum tower overhead products (the two streams which are combined to make up the process solvent) were conducted for the detection of trace metals. Higher concentrations of most metals were present in the fractionator bottoms which contained on the average 9.6 ppm iron, 1.7 ppm chromium, 0.7 ppm nickel, and 0.6 ppm silicon. On the average silicon and iron were present in the vacuum overhead product to the extent of 1.2 ppm and 0.4 ppm, respectively. The high iron and chromium levels in the fractionator bottoms are probably corrosion products.

b. Boiling Range Balances

In order to determine if the feed to the vacuum column underwent any change in boiling range, a theoretical boiling curve for the feed was constructed from the measured boiling curves for the overhead and bottoms products. This reconstructed boiling curve was then compared with the actually measured boiling curve of the vacuum column feed to see if there were any noticeable differences.

As Figures B-6 to B-8 show for the cases examined, there was generally good agreement between the two distillation curves. Thus, within experimental error, it can be concluded that little or no polymerization or cracking occurs in the vacuum column.

c. Vapor Velocity

The determination of the vapor velocity in the vacuum column was based on using the ideal gas law at the column temperature and pressure. The average molecular weight of the vapor was estimated from available data to be about 230. The nominal cross sectional area for vapor flow was taken to be 1.031 square feet. Using these values gives a calculated vapor velocity in the vacuum column of about 1 ft/s (including the recycled distillate).

5. Conclusions from the Vacuum Column Study

The information that was derived from the experimental work on the vacuum tower has led to the following observations:

- a. Vacuum tower bottoms is a non-Newtonian pseudo-plastic with thixotropic behavior.
- b. The viscosity of the vacuum tower bottoms increases with increasing flash zone temperature.
- c. The amount of distillate in the vacuum tower bottoms decreases with increasing flash zone temperature.
- d. The viscosity of vacuum tower bottoms increases with decreasing 900°F- distillate content.
- e. Vacuum tower bottoms do not polymerize or crack at temperatures in the range of 300-375°C.

D. Future Plans

During the fourth quarter, a 2² factorial experiment will be run to determine the effects of recycle solids level and hydrogen partial pressure of yields from Powhatan No. 5 Mine coal. Center point for this design will be Run 56.

A P P E N D I X A

SRC PILOT PLANT TABLES AND FIGURES

TABLE A-1

COAL PROCESSING SUMMARY

	Coal Processed, <u>Tons</u>	<u>On-Stream Time</u>		Available Operating Time <u>Adj. Hr. (b)</u>	<u>Average Feed Rate</u>		<u>On-Stream Factor</u>		
		<u>Days</u>	<u>Hours (a)</u>		<u>Tons per On-Stream Day</u>	<u>Pounds per On-Stream Hr (a)</u>	<u>Days, %</u>	<u>Hours, % (a)</u>	<u>Adjusted Hr., % (b)</u>
<u>1979</u>									
July	1,530	37	796	829	41.4	3,844	100.0	89.6	96.0
August	1,083	25	548	572	43.3	3,953	80.6	73.7	95.8
September	0	0	0	0	NA	NA	NA	NA	NA
Third Quarter	2,613	62	1,344	1,401	42.2	3,888	63.3	57.1	95.9
Second Quarter	1,812	54	1,138	1,209	33.6	3,185	58.7	51.5	94.1
First Quarter	693	37	654	1,516	18.7	2,119	41.1	30.3	43.1
Year to Date	5,118	153	3,136	4,126	33.5	3,264	54.6	46.7	76.0
Total 1978 ^(d)	5,572	225	4,320	6,102	24.8	2,580	62.8	50.3	70.8
Total 1977	4,776	216	3,990 ^(a)	---	22.1	2,115 ^(a)	59.2 ^(c)	69.9 ^(a)	---
Total 1976	6,559	234	---	---	28.0	---	63.9	---	---
Total 1975	8,021	241	---	---	33.3	---	66.0	---	---
Total 1974	678	30	---	---	22.3	---	32.6	---	---
Total	30,724	1,099	11,446 ^(a)	10,228 ^(b)	28.0	2,605	60.2	54.8 ^(a)	72.9 ^(b)

(a) Data accumulated since May 1, 1977.

(b) Data accumulated since January 1, 1978. Available operating time is adjusted for downtime not directly related to process problems or equipment failures.

(c) SRC-II on-stream factor was 81.9% based on days of operation from start on May 9 through end of 1977.

(d) Calculations based on data available from January 1, 1978 through December 24, 1978 (358 days).

TABLE A-2

Average Raw Coal Analyses, Wt%

	<u>July</u>		<u>August</u>
	<u>Colonial</u>	<u>Lafayette</u>	<u>Colonial</u>
	<u>Coal</u>	<u>Coal</u>	<u>Coal</u>
Ash	10.41	8.40	10.22
Moisture	6.66	4.59	5.87

TABLE A-3

Average Dried, Pulverized Coal Analyses, Wt%

	<u>July</u>		<u>August</u>
	<u>Colonial</u>	<u>Lafayette</u>	<u>Colonial</u>
	<u>Coal</u>	<u>Coal</u>	<u>Coal</u>
Carbon	70.77	73.53	70.62
Hydrogen	5.18	5.35	5.22
Nitrogen	1.54	1.59	1.50
Sulfur	3.86	2.85	3.67
Oxygen	7.54	7.62	8.12
Ash	10.59	8.45	10.36
Moisture	0.52	0.61	0.51
Iron in Ash	24.41	17.05	23.00
Iron (as rec.)	2.50	1.44	2.38
Chloride	0.04	0.19	0.02

TABLE A-4

Average Analyses For Forms of Sulfur, Wt%

	<u>July</u>		<u>August</u>
	<u>Colonial</u>	<u>Lafayette</u>	<u>Colonial</u>
	<u>Coal</u>	<u>Coal</u>	<u>Coal</u>
Pyritic Sulfur	2.26	1.30	2.02
Sulfate Sulfur	0.27	0.18	0.26
Organic Sulfur	1.33	1.37	1.39
Total Sulfur	3.86	2.85	3.67

TABLE A-5

Average Sieve Analysis of Dried, Pulverized Coal, Wt%

	<u>July</u>		<u>August</u>
	<u>Colonial Coal</u>	<u>Lafayette Coal</u>	<u>Colonial Coal</u>
- 40 Mesh	99.60	99.41	99.11
-100 Mesh	97.47	98.14	89.41
-140 Mesh	93.10	93.66	75.23
-200 Mesh	79.09	81.61	58.21

TABLE A-6

Typical Analysis of Stripper Bottoms, Wt%

	<u>July</u>		<u>August</u>
	<u>Colonial Coal; SRC-I</u>	<u>Lafayette Coal; SRC-I</u>	<u>Colonial Coal; SRC-I</u>
Water	0.16	0.20	NA*
Light Oil	0.06	0	NA*
Wash Solvent	0	0	NA*
Process Solvent	60.41	53.06	NA*
Vacuum Bottoms (P.I. Included)	39.37	46.74	42.23
Pyridine Insolubles (As Received)	7.25	8.11	7.65
Ash in Pyridine Insolubles	67.66	51.19	66.69

*Determination of these values was discontinued in August when it was determined they were no longer needed.

TABLE A-7

Average MAF Coal Conversion, Wt%

July

Colonial Coal	94.1
Lafayette Coal	92.0

August

Colonial Coal	94.2
---------------	------

TABLE A-8

Average Fractional Analyses of Liquid Products

<u>Distillation Fractions:</u>	<u>Light Oil</u>	<u>Wash Solvent</u>	<u>Process Solvent</u>
--------------------------------	------------------	---------------------	------------------------

July

IBP-380°F	91	17	0
380-480°F	9	82	1
480-850°F	0	1	99

August

IBP-380°F	90	13	0
380-480°F	10	87	0
480-850°F	0	0	100

TABLE A-9

Average Analysis of Pilot Plant Vacuum Bottoms, Wt%

	<u>July</u>	<u>August</u>
Carbon	75.21	74.33
Hydrogen	5.06	5.05
Nitrogen	1.76	1.70
Sulfur	2.10	2.27
Oxygen(bv difference)	2.90	2.90
Ash	12.97	13.75
Fusion Point, °F	336	318

TABLE A-10

Typical Analysis of Lummus Unit Vacuum Bottoms, Wt%*

	<u>July</u>	<u>August</u>
Carbon	84.19	86.77
Hydrogen	5.82	5.83
Nitrogen	2.09	2.06
Sulfur	0.51	0.81
Oxygen	6.93	3.58
Ash	0.46	0.95
Fusion Point, °F	331	314

*At various times, ash content of this product was less than 0.16%.

TABLE A-11

Process Waste Disposal Analyses

July

	<u>Bio Unit Feed</u>	<u>Bio Unit Effluent</u>	<u>Plant Effluent (composite)</u>
pH	6.8	6.3	7.0
Phenol, ppm	54	0.83	0.19
Chemical Oxygen Demand, ppm	1000	241	53
Biological Oxygen Demand, ppm	164	141	9.2
Total Suspended Solid, ppm	131	79	9
Nitrogen, ppm	52	32	-

August

	<u>Bio-Unit Feed</u>	<u>Bio Unit Effluent</u>	<u>Plant Effluent (composite)</u>
pH	6.9	6.6	6.8
Phenol, ppm	63	0.97	0.23
Chemical Oxygen Demand, ppm	869	344	104
Biological Oxygen Demand, ppm	149	23.4	14.5
Total Suspended Solids, ppm	140	77	46
Nitrogen, ppm	58	29	-

September

	<u>Bio Unit Feed</u>	<u>Bio Unit Effluent</u>	<u>Plant Effluent (composite)</u>
pH	6.3	6.4	6.9
Phenol, ppm	51.	0.60	0.14
Chemical Oxygen Demand, ppm	373	143	65
Biological Oxygen Demand, ppm	245	34	7.5
Total Suspended Solids, ppm	21	60	6.7

TABLE A-12

ANALYSIS OF SELECTED LUMMUS SAMPLES

<u>July</u>			
<u>Sample Type</u>	<u>Slurry Feed</u>	<u>Antisolvent Free Underflow</u>	<u>Antisolvent Free Overflow</u>
Toluene Insolubles, %	18.55	-	-
Pyridine Insolubles, %	6.87	18.15	0.75
Ash as Received, %	5.26	11.48	1.77
Distillation:			
IBP to 550°F, wt %	2.01	2.86	1.72
500 to 650°F, wt %	31.48	23.84	40.10
650 to 850°F, wt %	22.70	22.67	22.75
Above 850°F, wt %	43.81	50.63	35.43
<u>August</u>			
<u>Sample Type</u>	<u>Slurry Feed</u>	<u>Antisolvent Free Underflow</u>	<u>Antisolvent Free Overflow</u>
Toluene Insolubles, wt %	18.79	22.89	11.13
Heptane Insolubles, wt %	36.06	43.26	25.56
Pyridine Insolubles, wt %	7.55	16.79	0.47
Ash, (as rec'd), wt %	4.99	11.61	0.06
Distillation:			
IBP to 500°F, wt %	2.4	2.8	2.1
500 to 650°F, wt %	36.1	25.8	43.8
650 to 850°F, wt %	21.3	21.8	22.0
Above 850 °F, wt %	40.2	49.6	31.9

TABLE A-13

LAFAYETTE MINE, KENTUCKY NO. 9 COAL
PROXIMATE AND ULTIMATE ANALYSES

F-487

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 228 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 AREA CODE 312 726-8434



PLEASE ADDRESS ALL CORRESPONDENCE TO:
16130 VAN DRUNEN RD., SOUTH HOLLAND, IL 60473
OFFICE TEL. (312) 264-1173

THE PITTSBURG & MIDWAY COAL MINING CO.
P. O. Box 199
Dupont, WA 98327
Attn: R. E. Ferrussel and T.P. Witte

August 1, 1979

Kind of sample reported to us Coal, air-dried

Sample Identification by The Pittsburg & Midway Coal Mining

Sample Lafayette Mine



Sample # 1609
Kentucky #9 seam from
Lafayette Mine
Tag # 58039

Sample taken by The Pittsburg & Midway Coal

Date sampled 7/2/79 from pile.

Date received 7-17-79

P/O# T-4649

PROXIMATE ANALYSIS			Analysis report no. 71-35772		ULTIMATE ANALYSIS		
	As received	Dry basis			As received	Dry basis	% Weight
% Moisture	3.56	XXXXX			Moisture	3.56	XXXXX
% Ash	7.85	8.14			Carbon	72.69	75.37
% Volatile	37.95	39.35			Hydrogen	4.95	5.13
% Fixed Carbon	50.64	52.51			Nitrogen	1.51	1.57
	<u>100.00</u>	<u>100.00</u>			Chlorine	0.19	0.20
Btu/lb.	13077	13560			Sulfur	2.57	2.67
% Sulfur	2.57	2.67			Ash	7.85	8.14
% Alk. as Na ₂ O	XXXXX	0.16			Oxygen (diff)	6.68	6.92
						<u>100.00</u>	<u>100.00</u>
<u>SULFUR FORMS</u>			<u>MINERAL ANALYSIS OF ASH</u>				
% Pyritic Sulfur	0.98	1.02			Silica, SiO ₂		50.46
% Sulfate Sulfur	0.02	0.02			Alumina, Al ₂ O ₃		21.08
% Organic Sulfur	1.57	1.63			Titania, TiO ₂		1.00
<u>WATER SOLUBLE ALKALIES</u>					Ferric oxide, Fe ₂ O ₃		19.77
% Na ₂ O =	XXXXX	0.009			Lime, CaO		1.65
% K ₂ O =	XXXXX	0.006			Magnesia, MgO		0.83
<u>FUSION TEMPERATURE OF ASH</u>					Potassium oxide, K ₂ O		2.33
	Reducing	Oxidizing			Sodium oxide, Na ₂ O		0.39
Initial Deformation	2100 °F	XXXXX °F			Sulfur trioxide, SO ₃		0.91
H is Cone Height Softening (H=W)	2235 °F	XXXXX °F			Phos. pentoxide, P ₂ O ₅		0.08
W is Cone Width Softening (H = 1/2 W)	2370 °F	XXXXX °F			Undetermined		1.47*
Fluid	2500 °F	XXXXX °F					<u>100.00</u>
% EQUILIBRIUM MOISTURE =	3.67				SILICA VALUE =		69.40
HARDGROVE GRINDABILITY INDEX =					BASE: ACID RATIO		0.34
FREE SWELLING INDEX =	3 1/2				T ₂₅₀ Temperature =		2490 °F
*These ignited basis results were used to calculate undetermined value above					Respectfully submitted, COMMERCIAL TESTING & ENGINEERING CO.		
% Strontium oxide, SrO		0.00			 R. A. HOUSER, Manager, Midwest Division		
% Barium oxide, BaO		0.01					
% Manganese oxide, Mn ₂ O ₄		0.02					
Fouling Index		0.13					
Original Copy Watermarked For Your Protection		Slagging Index		1.04	 Charter Member		

RAE/br

80. HOLLAND, IL • BILLINGS, MT • BIRMINGHAM, AL • CHARLESTON, WV • CLARKSBURG, WV • CLEVELAND, OH • DENVER, CO • GOLDEN, CO
MENDOTON, KY • MIDDLESBORO, KY • MOBILE, AL • NEW ORLEANS, LA • NORFOLK, VA • PINEVILLE, KY • VANCOUVER, B.C. CAN.

TABLE A-14

LAFAYETTE MINE, KENTUCKY NO. 9
COAL MACERAL ANALYSES

IAD BATCH NUMBER: 97-C968-019-01 Lafayette Mine, KY No. 9 Coal

REPORT OF ANALYSIS ON SAMPLE: 71-35772

8/ 1/79

MACERAL ANALYSIS
(VOLUME PERCENT)
(MINERAL-MATTER CONTAINING BASIS)

MACERAL		MACERAL GROUP	
VITRINITE	65.5	VITRINITE	72.2
PSEUDOVITRINITE	6.7		
EXINITE	3.5	EXINITE (LIPTINITE)	7.4
RESINITE	3.9		
SEMI-FUSINITE*	4.2		
SEMI-MACRINITE*	0.3		
FUSINITE	3.5	INERTINITE	15.3
MACRINITE	0.2		
MICRINITE	7.1		
MINERAL MATTER**	5.1		5.1
TOTAL	100%		100%

TOTAL REACTIVES- 81.1
TOTAL INERTS- 18.9

◆◆◆◆◆◆◆◆◆◆

* CONSIDERED 1/3 REACTIVE, 2/3 INERT FOR PURPOSES OF
COKE STABILITY PREDICTIONS.

** CALCULATED FROM 8.14 % DRYASH, 2.67 % DRY SULFUR

COMMERCIAL TESTING & ENGINEERING CO.

Original Copy Watermarked
For Your Protection

9-686



TABLE A-15
SHORT RESIDENCE TIME SRC II TEST
REACTION CONDITIONS

Raw Coal Feedrate, lb/hr	1614
M.F. Coal Feedrate, lb/hr	1551
Coal Space Rate Per Dissolver Volume, lb/hr/ft ³	31.0
Seal Flush Rate, lb/hr	989
Recycle Slurry Rate, lb/hr	3652
Total Slurry Rate to Reactor, lb/hr	6192
Nominal Slurry Reactor Residence Time, hours	0.58
Feed Slurry Coal Concentration, % wt	25.0
Dissolver Outlet Temperature, °F	843
Dissolver Top Pressure, psig	1991
Total Gas To Reaction Area, lb/hr	917
Total Gas Hydrogen Concentration, % volume	87
Vacuum bottoms Melt Point, °F	352
Run Duration, hours	45.5

TABLE A-16
SHORT RESIDENCE TIME SRC II TEST
ESTIMATED PRODUCT YIELDS

<u>COMPONENT</u>	<u>YIELD, % MFC</u>	<u>YIELD, % MAFC</u>
H ₂	-2.2	-2.5
C ₁	5.0	5.7
C ₂	3.3	3.7
C ₃	2.6	3.0
C ₄	1.4	1.6
CO	0.8	0.9
CO ₂	1.4	1.6
H ₂ S	1.7	1.9
Light Oil (Ambient to 380°F)	3.7	4.2
Wash Solvent (380°-480°F)	8.7	9.9
Process Solvent (480°F plus)	7.1	8.0
Ash	11.7	-
Organic Vacuum Bottoms	52.1	59.0
Water (by Difference)	2.7	3.0

} 12.3

} 14.0

} 19.5

} 22.1

TABLE A-17

LIMITATIONS ON ROTOVISCO OPERATING RANGE

MEASURING HEAD → ROTOR ↓		SHEAR RATE (sec ⁻¹)			
		COARSE - DMK 500		FINE - DMK 50	
		Published Limitations	Latest Recommendation	Published Limitations	Latest Recommendation
40.8 mm dia. (MV I)	HIGH	2340	1170	2340	Do Not Use
	LOW	0.234	0.234	0.234	Do Not Use
36.8 mm dia. (MV II)	HIGH	900	450	900	Do Not Use
	LOW	0.09	0.09	0.09	Do Not Use

MEASURING HEAD → ROTOR ↓		TORQUE (dynes/cm ²)			
		COARSE - DMK 500		FINE - DMK 50	
		Published Limitations	Latest Recommendation	Published Limitations	Latest Recommendation
40.08 mm dia. (MV I)	HIGH	2850	2850	303	Do Not Use
	LOW	142	142	15.2	Do Not Use
36.8 mm dia. (MV II)	HIGH	3370	3370	359	Do Not Use
	LOW	168	168	18.0	Do Not Use

TABLE A-18

ACTUAL AND PREDICTED EFFECTS OF SOLIDS ON SLURRY VISCOSITY

F_s	$\phi_s(1)$	Actual μ_m	μ_m/μ_ℓ			Actual Mooney C Factor ⁽²⁾ Calculated From Data
			Actual	Predicted By Kunitz	Predicted By Mori	
0.0	0.0	83.0	1.00	1.00	1.00	-
0.10	0.0485	90.3	1.09	1.25	1.16	-8.39
0.20	0.103	124.	1.49	1.62	1.38	3.44
0.30	0.164	202.	2.43	2.22	1.72	3.28
0.40	0.234	381.	4.59	3.24	2.28	2.63

Solid - Mineral Residue

Liquid - Process Solvent

μ_ℓ Liquid Viscosity [cP]

μ_m Mixture Viscosity [cP]

μ_m/μ_ℓ Relative Viscosity [dimensionless]

ρ_s

Solid Density, 2.30 gm/cc

ρ_ℓ

Liquid Density, 1.055 gm/cc

F_s

Weight Fraction Solids =

(wt % solids)/100

ϕ_s

Volume Fraction Solids

$$(1) \phi_s = \left[1 + \left(\frac{1}{F_s} - 1 \right) \left(\frac{\rho_s}{\rho_\ell} \right) \right]^{-1}$$

$$(2) C = \left[\frac{1}{\phi_s} - \frac{2.5}{\ln(\mu_m/\mu_\ell)} \right]$$

TABLE A-19

COMPARISON COMPOSITION AND VISCOSITY OF 208 SAMPLES

	<u>5/27/79</u>	<u>5/28/79</u>	<u>% CHANGE</u>
TIME SAMPLED	0800	0400	
SAMPLE NUMBER	113101	113124	
% PYRIDINE INSOLUBLE	25.45	25.23	-0.51
% ASH IN P.I.	69.81	69.48	-0.47
W/W DIST. I.B.P.	526	486	-7.60
5%	602	605	0.50
10%	638	632	-0.94
VAC. Dist., mmHg	2.0	2.0	(0.00)
% WATER	0.15	0.12	-20.00
% NAPHTHA	0.0	0.0	0.00
% MIDDLE DIST.	0.86	0.78	-9.30
% HEAVY DIST.	18.81	18.48	-1.75
% VAC. BOTTOMS	80.18	80.62	-0.55
ENDPOINT °C	252	230	(-8.73)
ENDPOINT, mmHg	6.0	5.0	(-16.67)

VISCOSITY, cp*

TEMPERATURE

285°F	-	452.5
295	424.0	291.5
305	266.0	211.5
315	197.5	-

*All measurements taken with Brookfield viscometer model HA, spindle 21 at 186 sec⁻¹ shear rate.

TABLE A-20

REACTION AREA TRANSIT TIMES FOR RADIOISOTOPE TRACER INJECTIONS
(all times are in minutes)

<u>Radioisotope</u>	<u>Preheater Plus Transfer Line</u>		<u>Dissolver</u>	
	<u>Start of Peak</u>	<u>End</u>	<u>Start of Peak</u>	<u>67% Past Detector</u>
Argon (Ar-41) (5 injects)	3.5-4.0	5.0-5.5	4.5-5.0	6.0-6.5
Bromophenanthrene (Br-82)	11	14	15-16*	Not Taken
	11.5	15	17	30+
	11.7	14	14	60+
Gold (Au-198) Colloidal Form	10.5	14	15*	No Peak
	Flake Form (10-40)	16*	20*	--No discernible peak--

*These responses were so small that the data must be considered rough approximations.

FIGURE A-1

SRC I SOLVENT INVENTORY

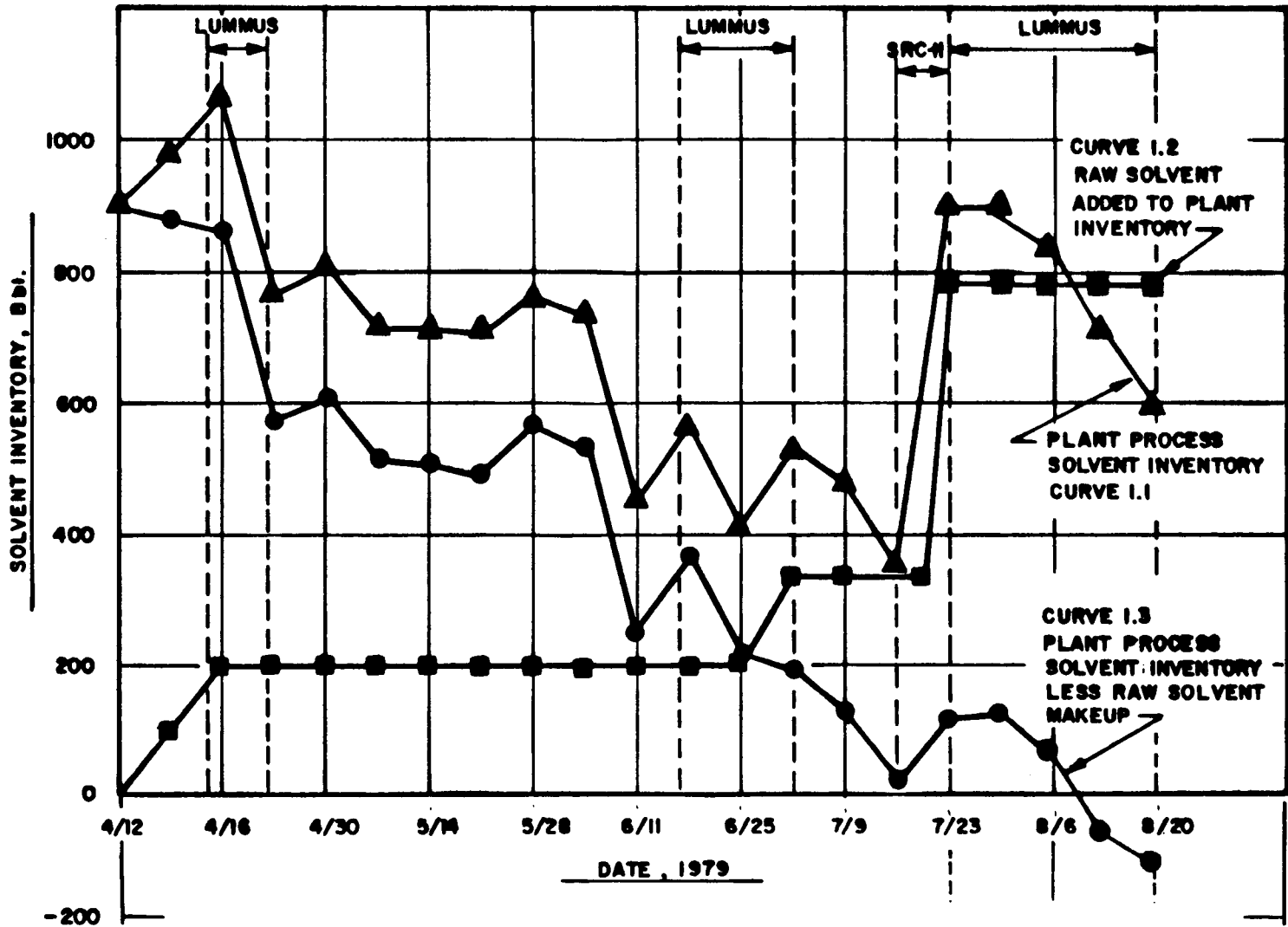


FIGURE A-2

LIMITATIONS ON ROTOVISCO OPERATING RANGE

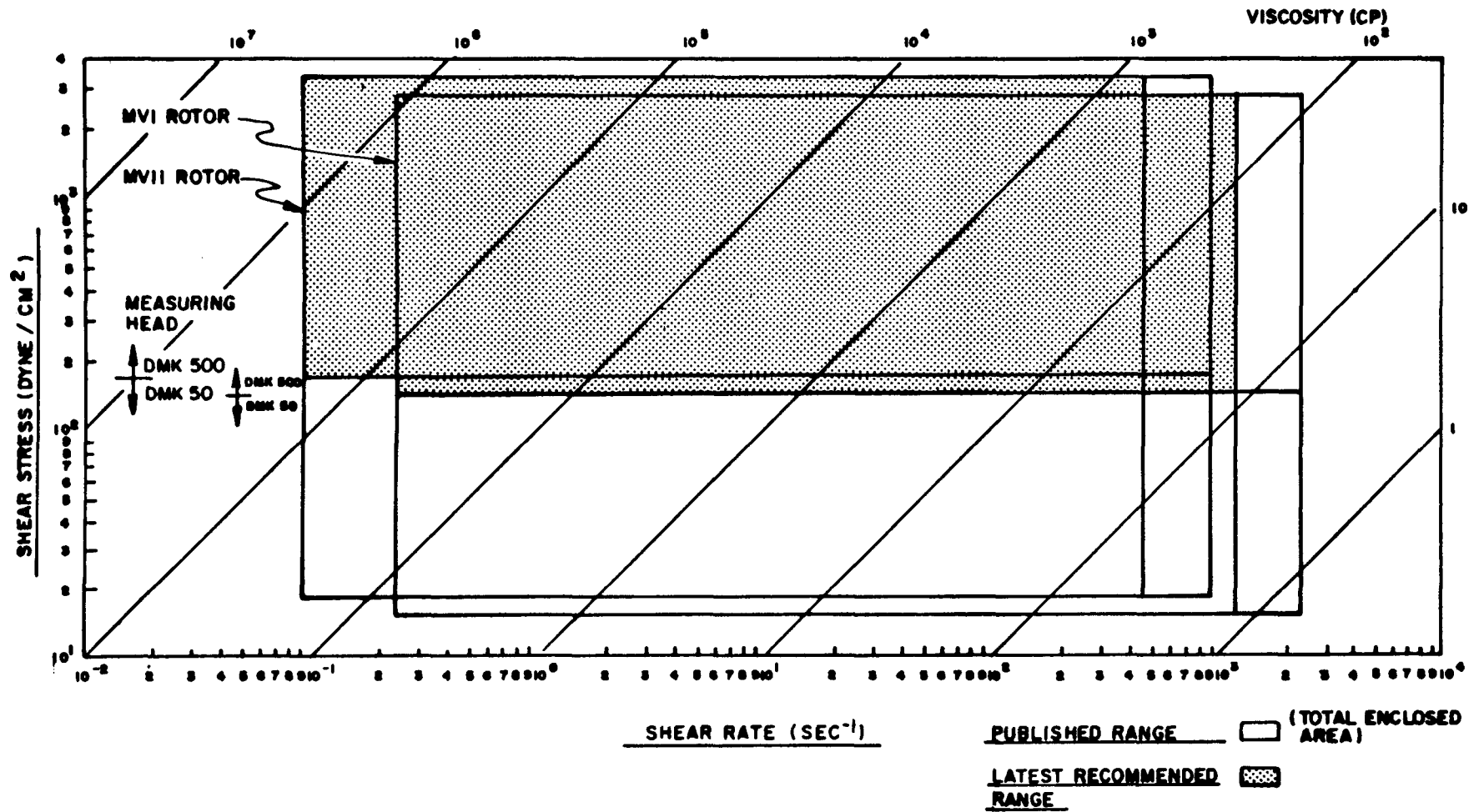


FIGURE A-3

COMPARISON OF EXPERIMENTAL DATA AND ESTIMATES
FOR SOLIDS EFFECT ON VISCOSITY IN ARTIFICIAL SLURRY

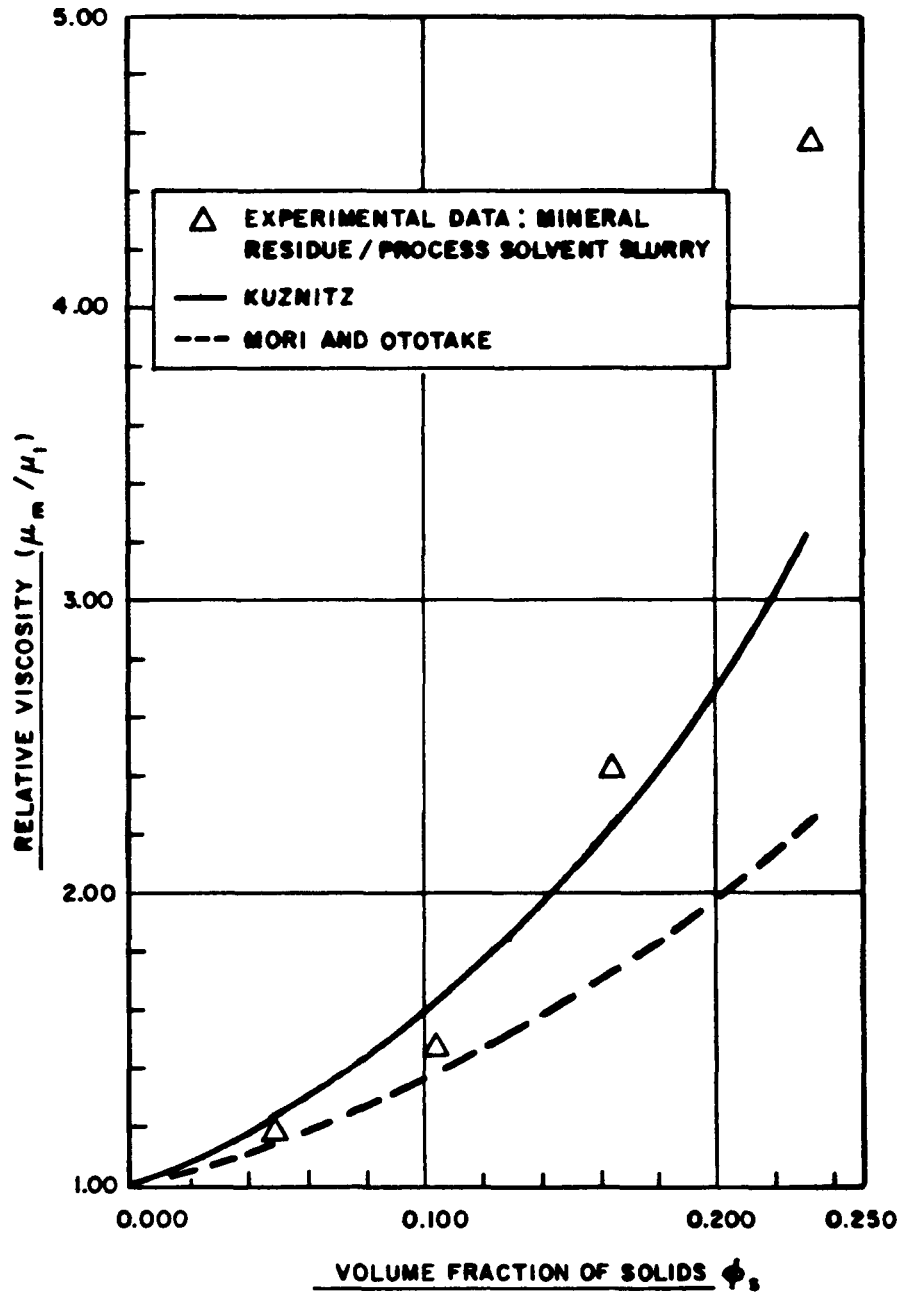
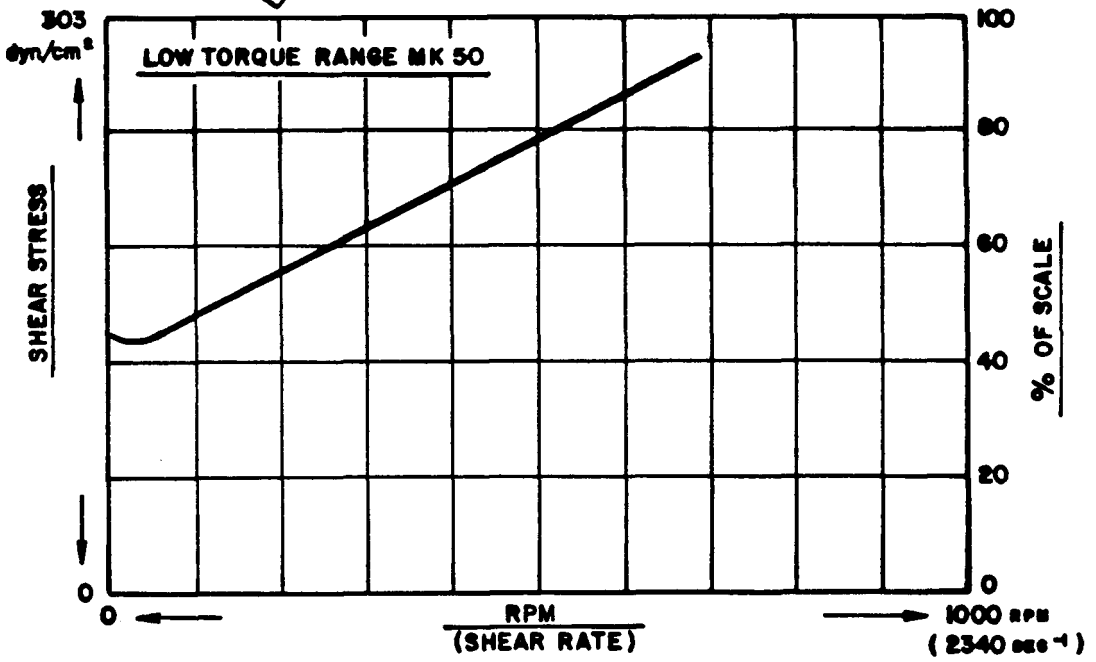
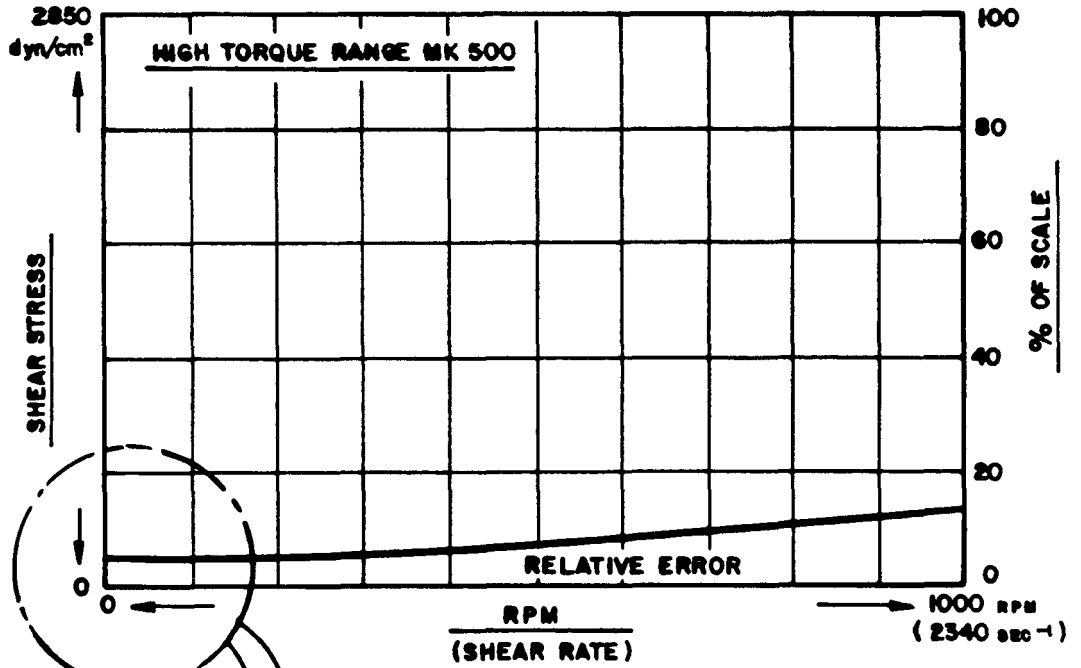


FIGURE A-4

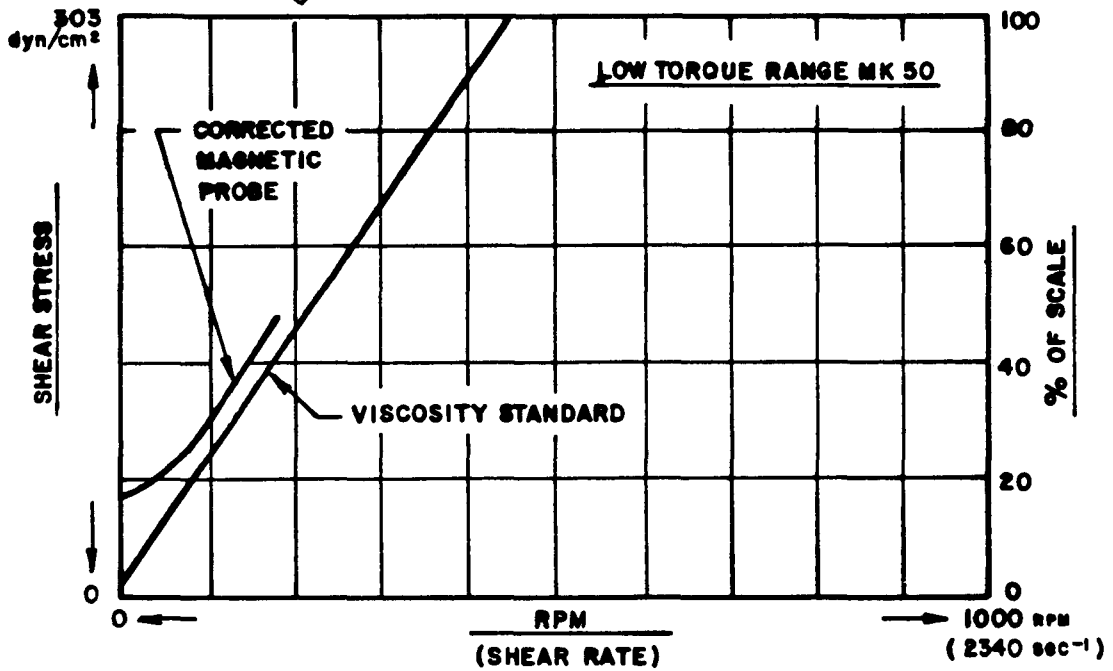
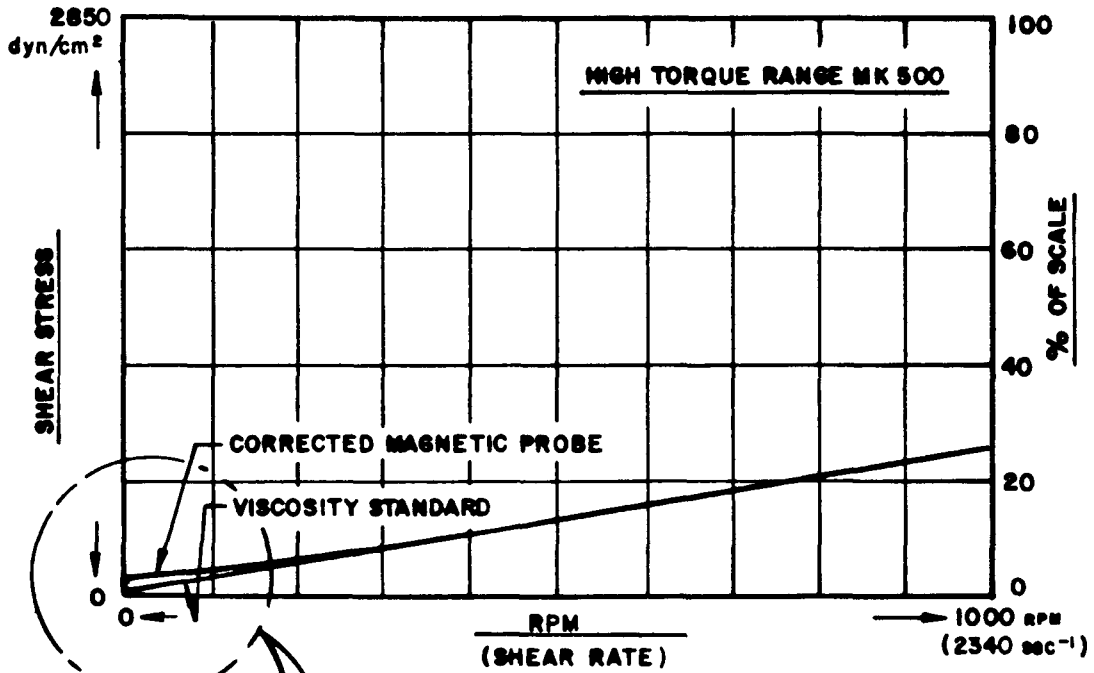
TORQUE ERROR INTRODUCED BY MAGNETIC DRIVE PROBE



NOTE: ABOVE MEASUREMENTS MADE WITHOUT SAMPLE

FIGURE A-5

COMPARISON OF CORRECTED MAGNETIC DRIVE PROBE DATA
WITH VISCOSITY STANDARD DATA



NOTE: ABOVE MEASUREMENTS MADE WITH STANDARD SAMPLE

FIGURE A-6

LETDOWN VALVE POSITION, FLOW RATE, PRESSURE DIFFERENTIAL VS. TIME

LCV-175A 1" DBAQ

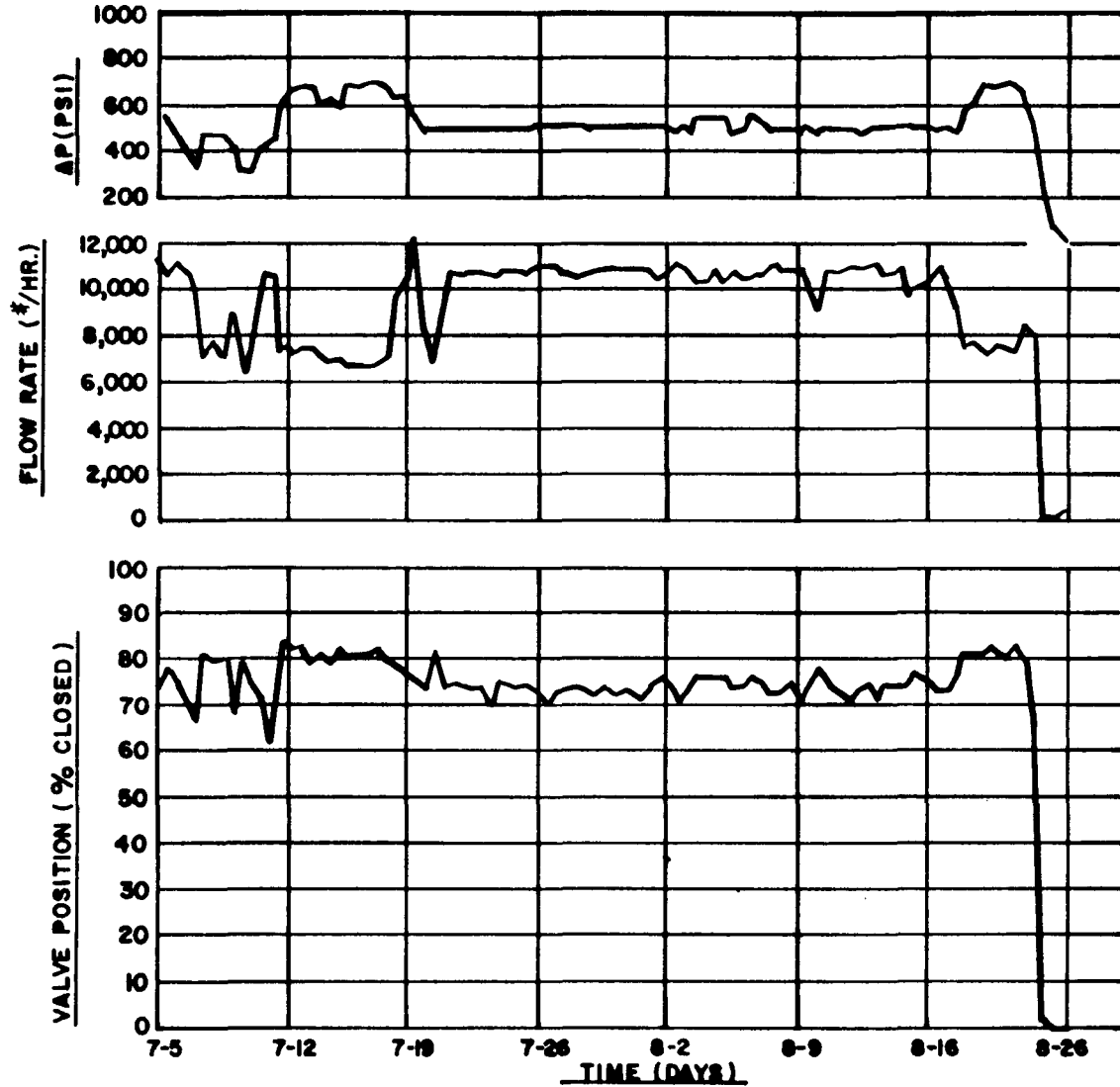


FIGURE A-7

FISHER VALVE TRIM ASSEMBLY (LCV-166 A)

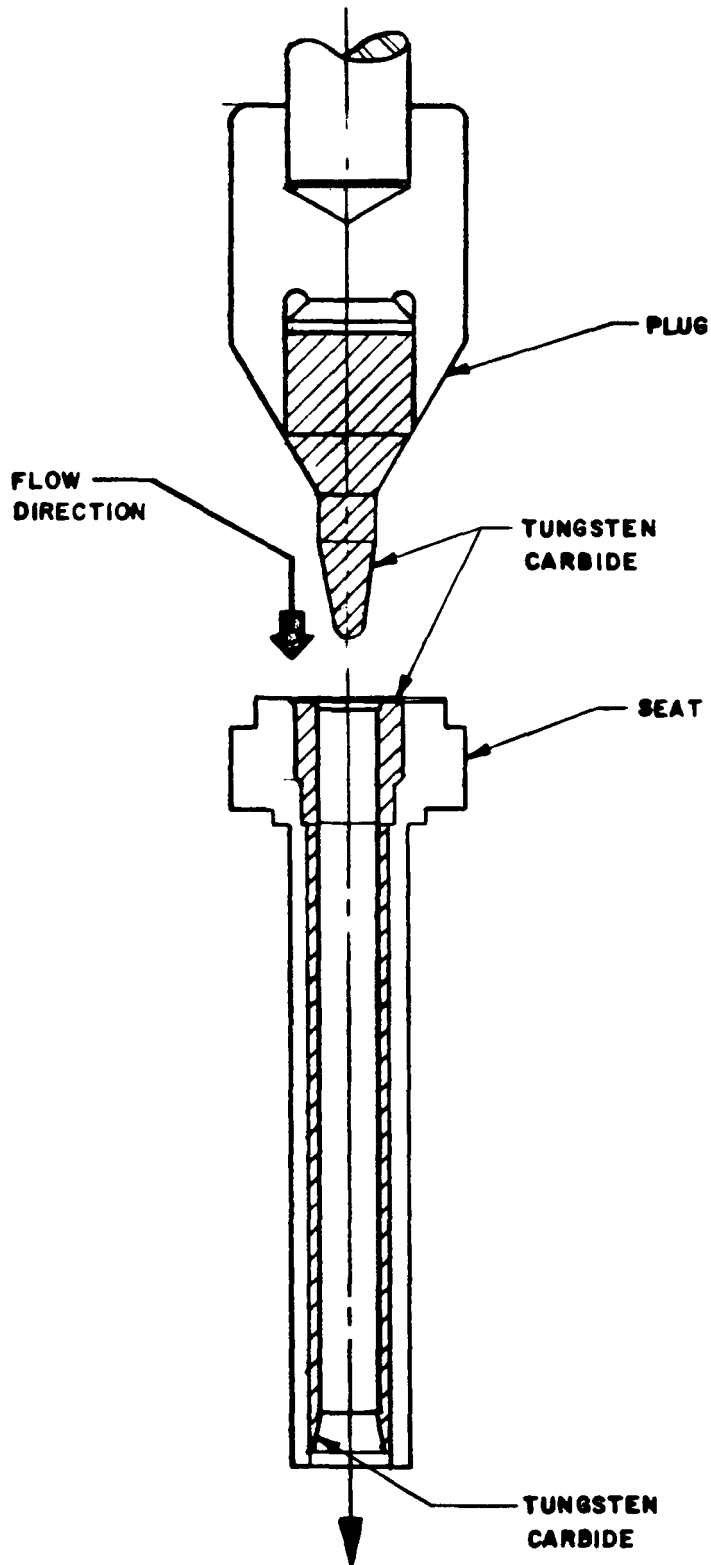


FIGURE A-8

WILLIS VALVE TRIM (LCV-166B)

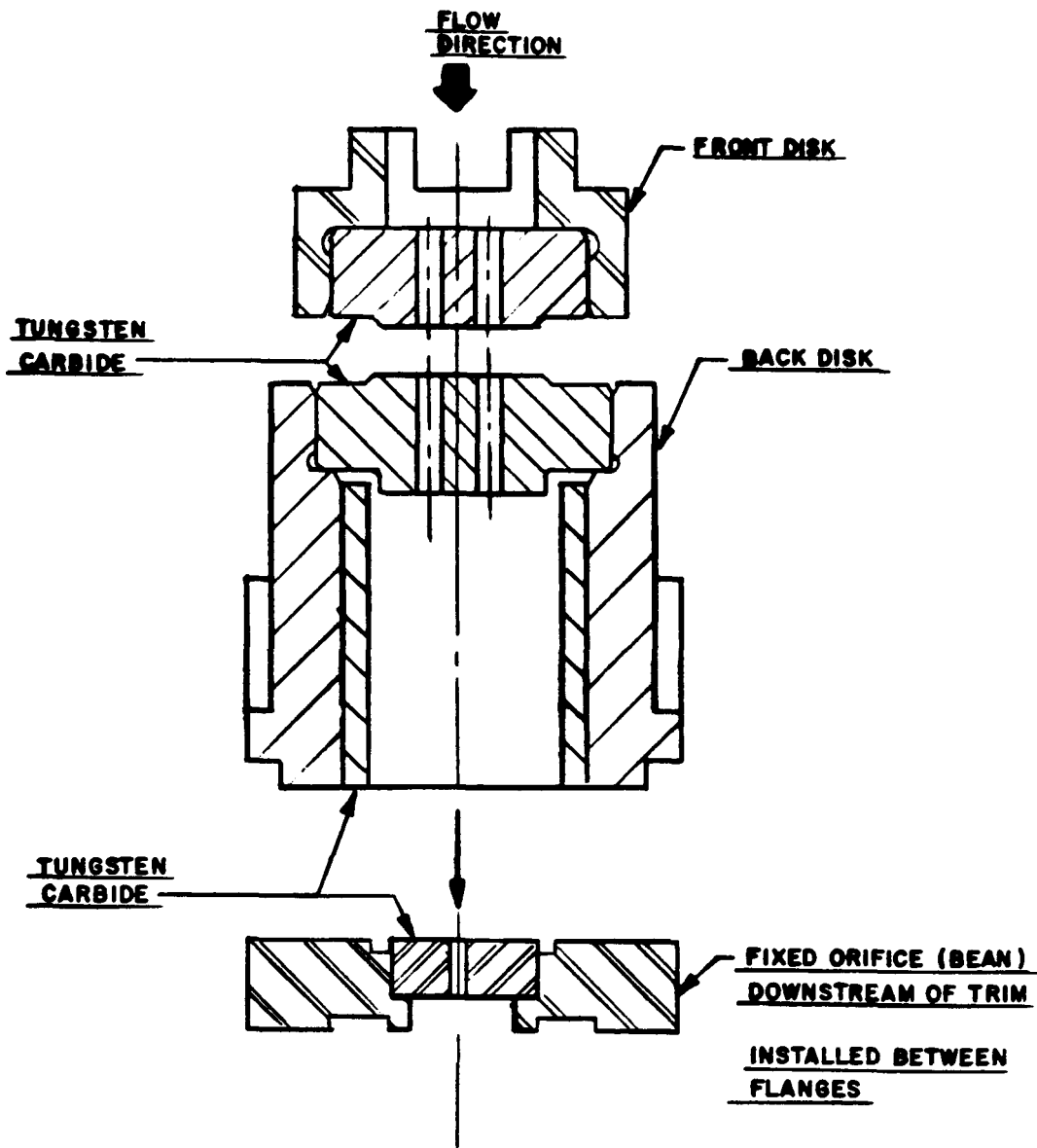
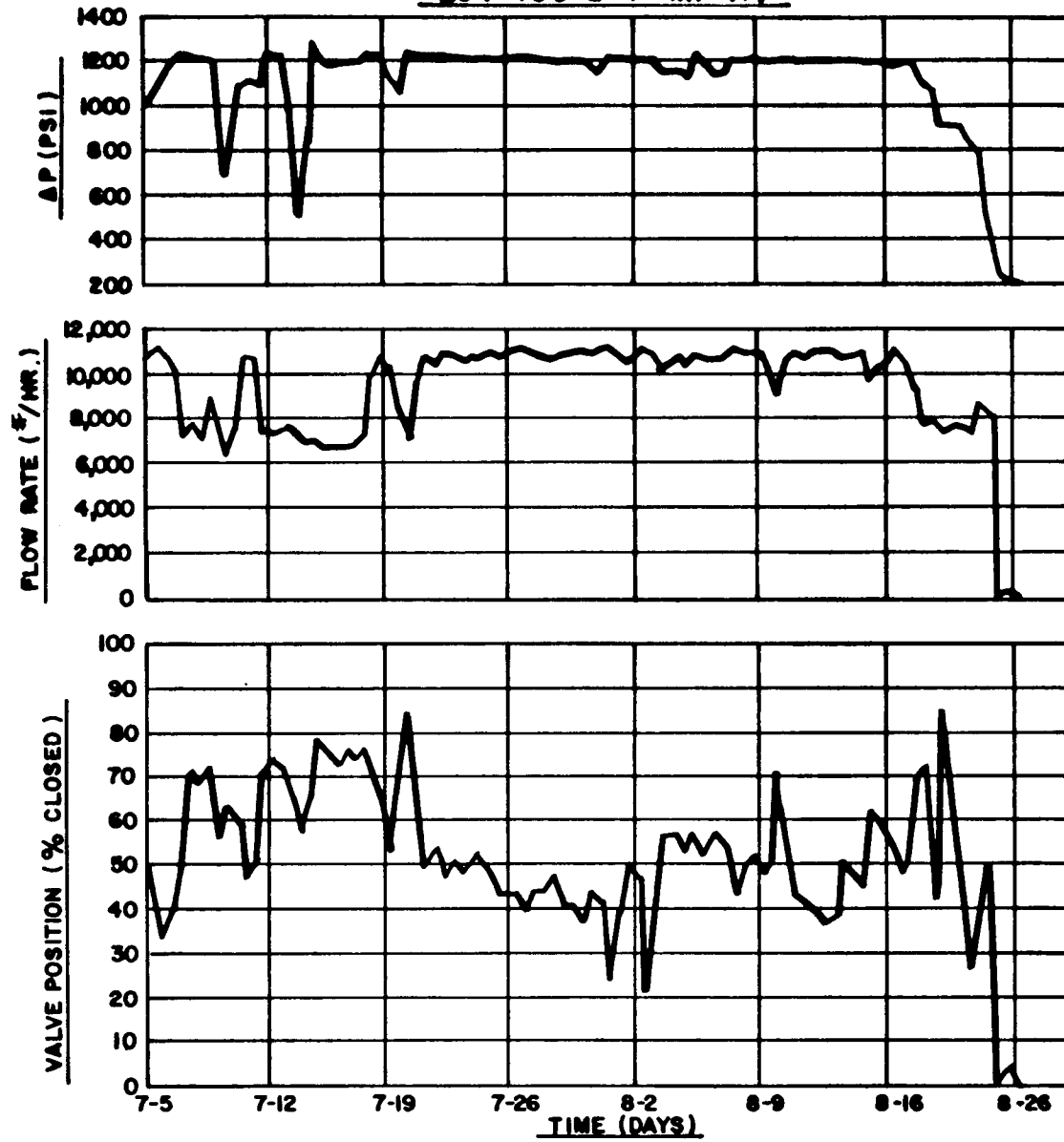


FIGURE A-9

LETDOWN VALVE POSITION, FLOW RATE, PRESSURE DIFFERENTIAL VS. TIME

LCV-166 B 1" MI-HT



A P P E N D I X B

PROCESS DEVELOPMENT UNIT P-99 TABLES AND FIGURES

Table B-1

PROPERTIES OF FOURTH SHIPMENT
OF POWHATAN NO. 5 MINE COAL (LR-26982)

Elemental Analysis* (moisture free), Wt %	
Carbon	70.28
Hydrogen	4.92
Nitrogen	1.24
Sulfur	3.52
Oxygen	13.33
Chlorine	0.05
Metals**	6.66
Ash	12.55
Moisture	1.36
Spectral Ash, Wt % of Ash	
Aluminum	10
Calcium	1
Iron	15
Magnesium	1
Potassium	1
Silicon	20
Sodium	0.2
Titanium	1
Particle Size Distribution, Wt %	
On 80 mesh	0
Through 80 on 200 mesh	4
Through 200 on 325 mesh	24
Through 325 on 625 mesh	36
Through 625 mesh	36

*Values used in preliminary material balance calculations.

**By difference

Table B-2

OPERATING CONDITIONS FOR RUNS 56 AND 57
MADE IN PDU P-99

Run No., P99-	56	57
Dissolver Pressure, psig	2000	2500
Average Dissolver Temperature, °F	851	851
Nominal Slurry Residence Time, hr	1.0	1.0
Feed Composition, Wt %		
Coal	30.5	30.3
Recycle Solids	13.7	14.5
Inlet Gas Purity, %	85	85
Total Dissolver Gas Rate, MSCF/T Feed Coal	58.9	59.1

Table B-3

SRC-II YIELDS* FOR RUNS MADE ON PDU P-99

Run No., P99-	56	57
Yields, Wt % of Moisture Free Feed Coal		
Hydrogen	-4.2	-4.7
Methane	5.5	5.0
Ethane	4.1	4.2
Propane	4.1	4.6
Isobutane	0.2	0.2
N-Butane	2.1	2.5
	<hr/>	<hr/>
Total C ₁ -C ₄ Gas	16.0	16.5
Ammonia	0.4	0.5
Hydrogen Sulfide	2.4	2.4
Carbon Dioxide	0.7	0.7
Carbon Monoxide	0.2	0.2
	<hr/>	<hr/>
Total Other Gases	3.7	3.8
Water	6.4	6.6
C ₅ -380°F	7.2	7.9
380-550°F	15.1	14.7
550-900°F	14.2	18.7
	<hr/>	<hr/>
Total C ₅ -900°F Distillate	36.5	41.3
900°F+ Pyridine Solubles	23.2	19.2
Insoluble Organic Matter	5.9	4.8
Ash	12.5	12.5
	<hr/>	<hr/>
Total 900°F+ Product	41.6	36.5

 *These results should still be considered preliminary, and finally issued yields may differ slightly from those shown.

Table B-4

INSPECTIONS FOR SRC-II NAPHTHA FEEDSTOCK

Distillation Cutpoint	300°F	350°F	375°F	400°F
LR Number	26239	26440	26441	26442
Gravity, °API	51.6	43.4	38.5	35.8
Nitrogen, Wt %	0.26	0.31	0.38	0.48
Nitrogen, Basic, ppm	530	1350	2175	3550
Sulfur, Wt %	0.07	0.11	0.12	0.25
Oxygen, Wt %*	0.9	2.1	2.9	3.5
FIA Hydrocarbon Analysis, Vol %**				
Aromatics	17.0	29.5	36.0	45.0
Olefins	6.5	5.5	4.5	4.0
Saturates	76.5	65.0	59.5	51.0
Distillation, D86, °F				
Overpoint	--	154	154	154
Endpoint	320	--	386	402
10%	--	210	210	220
30%	206	242	252	274
50%	224	276	296	324
70%	244	308	326	354
90%	276	342	354	378
Hydrocarbon Analysis, D2789, Vol %				
Paraffins	32.5	29.0	25.6	22.4
Monocycloparaffins	45.0	37.1	32.5	27.6
Dicycloparaffins	5.4	5.5	7.5	7.7
Alkylbenzenes	17.1	26.1	28.1	28.5
Benzene	1.7	1.5	1.6	2.0
Toluene	6.8	6.2	5.5	5.0
C ₈ Alkylbenzenes	7.7	9.3	8.6	8.0
C ₉ "	0.9	6.7	6.9	6.2
C ₁₀ "	0.0	2.1	4.0	4.1
C ₁₁ "	0.0	0.3	1.2	2.5
C ₁₂ "	0.0	0.0	0.3	0.6
Indanes & Tetralins	0.1	2.2	5.9	12.0
Naphthalenes	0.0	0.9	0.4	1.8

* Oxygen by difference

** May be in error due to High Phenol Content

Table B-5

P-99 VACUUM COLUMN OPERATION							
Period, P99-	Net Feed Rate, kg/h	Distillate * in Feed, Wt%	VTB, kg/h	Distillate * in VTB, Wt%	Net VTO, kg/h	Distillate * in VTO, Wt%	Flash Zone Temp., °C
54-3	11.69	30.24	8.38	8.58	3.31		324
54-4	12.78	31.30	9.45	8.53	3.33	91.90	320
54-5	14.00	27.85	10.00	5.88	4.00	89.15	333
54-7	12.14	28.39	8.36	5.30	3.78		344
54-8	13.59	29.66	9.64	4.74	3.95	88.63	340
54-9	14.29	30.36	9.94	3.34	4.35	95.37	348
54-10	14.24	32.69	9.11	3.58	5.13	93.55	351
54-11	15.12	35.12	10.06	4.68	5.06	88.91	359
54-12A	12.45	30.52	8.48	4.25	3.97	87.19	364
54-12B	13.27	30.22	9.23	3.66	4.04	86.62	368
55-0	9.43	29.07	6.62	3.40	2.81	86.34	369
55-1	12.40	28.65	8.91	5.09	3.49	86.92	364
55-2	10.06	27.16	7.10	4.70	2.96	88.02	368
55-3	11.67	25.71	8.36	3.60	3.31	89.43	367
55-4	12.15	21.86	9.24	4.58	2.91	96.30	365
55-5A	10.55	21.76	7.89	3.84	2.66	94.51	367
55-5B	11.26	23.40	8.70	4.50	2.56	87.77	368
55-6	12.68	27.81	9.38	4.33	3.30	85.98	372
55-7	11.90	24.32	8.86	2.90	3.04	91.87	375

*Distillate refers to distillate boiling below 900°F.

Table B-6

VISCOSITY* OF VACUUM TOWER BOTTOMS
475°F

Period, P99-	Shear Rate, sec ⁻¹						
	8.400	3.360	1.680	.840	.420	.168	.084
54-3	1,836	2,595	3,850	6,000	9,800	19,500	35,800
54-4	1,808	2,695	4,000	6,420	10,960	25,200	47,600
54-5		4,390	6,210	9,500	15,680	31,400	58,000
54-7					30,360	50,500	92,000
54-8				16,320	24,360	47,100	83,000
54-9						61,700	102,800
54-10						76,000	114,200
54-11						64,100	95,800
54-12A						83,000	128,800
54-12B						83,200	126,000
55-0					31,280	58,100	103,000
55-1				14,120	21,200	41,100	72,800
55-2						69,100	108,800
55-3						82,300	128,800
55-4					39,200	64,200	103,200
55-5A						85,400	138,800
55-5B						79,300	136,000
55-6					33,120	60,000	103,000
55-7						70,900	109,800

*All viscosities are reported in centipoise

Table B-7

VISCOSITY* OF VACUUM TOWER BOTTOMS
500°F

Period, P99-	Shear Rate, sec ⁻¹						
	8.400	3.360	1.680	.840	.420	.168	.084
54-3	1,236	1,935	3,040	4,920	8,440	18,000	38,400
54-4	1,272	2,045	3,200	5,380	9,200	19,200	38,800
54-5		3,295	4,960	7,900	13,400	27,200	51,400
54-7			8,500	12,800	20,440	39,600	73,800
54-8		4,885	7,270	11,100	18,160	37,100	65,600
54-9			8,920	13,560	21,960	48,000	78,200
54-10				15,280	24,520	46,800	82,200
54-11		4,445	6,460	9,960	16,240	33,400	60,600
54-12A				17,200	28,000	54,200	100,400
54-12B				15,760	25,400	50,700	89,200
55-0			9,570	14,520	23,760	47,400	88,000
55-1		4,330	6,300	9,720	15,760	32,900	58,800
55-2			8,790	13,420	21,840	45,100	83,600
55-3				17,700	28,040	51,500	103,800
55-4			9,300	14,300	23,000	45,400	89,600
55-5A				18,680	30,000	58,100	107,800
55-5B				17,880	29,600	60,300	114,000
55-6			9,150	14,100	23,640	47,900	87,200
55-7				15,640	24,920	48,000	84,800

*All viscosities are reported in centipoise

Table B-8

VISCOSITY* OF VACUUM TOWER BOTTOMS
525°F

Period, P99-	Shear Rate , sec ⁻¹						
	8.400	3.360	1.680	.840	.420	.168	.084
54-3	958	1,650	2,650	4,600	8,320	18,000	33,800
54-4	996	1,635	2,840	4,840	8,800	19,100	35,800
54-5	1,548	2,515	3,950	6,700	11,640	25,500	53,800
54-7		4,185	6,210	10,040	16,760	35,500	66,800
54-8		3,710	5,660	9,280	15,440	33,500	64,000
54-9		4,490	6,650	10,420	17,840	37,000	68,600
54-10		4,075	6,200	10,040	17,040	37,200	69,200
54-11		3,600	5,350	8,420	14,280	29,600	54,000
54-12A			7,810	12,700	21,400	45,000	82,000
54-12B		4,950	7,470	11,920	20,200	41,900	76,600
55-0		4,765	7,150	11,300	18,560	38,400	69,000
55-1		3,225	4,910	7,840	13,640	29,000	54,200
55-2		4,400	6,650	10,500	17,600	36,500	68,200
55-3			8,510	13,340	22,200	45,400	86,600
55-4		4,125	6,400	10,220	17,000	36,800	72,200
55-5A			9,010	15,820	24,200	51,000	92,200
55-5B			8,760	14,220	24,400	50,800	92,400
55-6		4,600	6,980	11,320	18,840	38,700	76,200
55-7			7,560	11,960	19,600	39,000	73,400

*All viscosities are reported in centipoise

Table B-9

VISCOSITY* OF VACUUM TOWER BOTTOMS
550°F

Period, P99-	Shear Rate, sec ⁻¹						
	8,400	3,360	1,680	.840	.420	.168	.084
54-3	802	1,545	2,400	4,380	7,680	16,600	28,400
54-4	814	1,510	2,600	4,680	8,240	18,300	35,000
54-5	1,266	2,145	3,660	6,320	11,200	23,500	43,400
54-7		3,365	5,220	8,600	14,800	32,200	55,200
54-8	1,698	2,830	4,510	7,500	13,200	27,500	56,000
54-9		3,575	5,420	8,800	15,000	32,400	63,800
54-10	1,874	3,105	4,990	8,420	14,640	31,900	58,800
54-11	1,628	2,755	4,400	7,340	12,840	27,000	47,000
54-12A		4,000	6,340	10,500	18,120	38,100	74,400
54-12B		3,895	6,030	9,920	17,040	37,400	68,000
55-0		3,555	5,550	9,140	15,600	34,600	61,400
55-1	1,512	2,520	4,050	6,800	11,840	26,200	49,000
55-2		3,375	5,300	8,800	15,600	33,900	64,600
55-3		4,275	6,580	10,720	18,120	38,500	71,600
55-4	1,940	3,270	5,220	8,620	15,040	34,100	58,600
55-5A		4,510	7,100	11,820	20,680	43,900	80,400
55-5B		4,425	7,000	11,900	20,920	44,000	82,800
55-6		3,695	5,800	9,580	16,400	35,000	67,600
55-7		3,930	6,060	9,900	17,080	36,800	64,000

* All viscosities are reported in centipoise

Table B-10

VISCOSITY* OF VACUUM TOWER BOTTOMS
575°F

Period, P99-	Shear Rate , sec ⁻¹						
	8.400	3.360	1.680	.840	.420	.168	.084
54-3	Not Tested at These Conditions						
54-4	Not Tested at These Conditions						
54-5	Not Tested at These Conditions						
54-7	1,518	2,745	4,360	8,100	14,400	31,400	45,200
54-8	1,400	2,420	4,000	6,900	12,200	25,300	45,400
54-9	1,562	2,705	4,400	7,580	13,840	29,400	52,200
54-10	1,524	2,615	4,440	7,500	13,000	30,500	55,000
54-11	1,264	2,190	3,660	6,200	11,040	23,800	40,000
54-12A	1,810	3,200	5,410	9,480	17,160	35,900	67,200
54-12B	1,722	3,020	4,960	8,460	15,080	33,200	59,000
55-0	1,584	2,715	4,450	7,700	14,000	30,300	53,000
55-1	1,174	2,075	3,500	6,040	10,320	22,400	40,000
55-2	1,588	2,750	4,520	7,740	14,280	31,600	54,800
55-3	1,970	3,345	5,410	9,020	16,120	35,700	65,200
55-4	1,500	2,630	4,380	7,700	14,200	29,500	50,800
55-5A		3,690	5,990	10,240	18,000	36,700	77,200
55-5B		3,610	6,050	10,220	18,840	40,800	75,000
55-6	1,678	2,950	4,910	8,420	14,600	33,000	60,600
55-7	1,734	2,970	4,860	8,240	14,680	32,500	54,600

*All viscosities are reported in centipoise

Table B-11

VISCOSITY OF FLASH TOWER BOTTOMS FOR RUN P99-55

<u>Sample Temp., °F</u>	<u>Shear Rate, sec⁻¹</u>	<u>Viscosity, cP</u>		
		<u>P99-55-5</u>	<u>P99-55-6</u>	<u>P99-55-7</u>
450	16.8	234	211	120
	8.4	316	238	170
	3.36	540	370	300
	1.68	890	540	460
	0.84	1,580	800	720
	0.42	2,840	1,080	1,400
	0.168	6,000	2,400	2,800
	0.084	12,000	5,800	4,000
475	16.8	181	123	112
	8.4	268	180	158
	3.36	500	325	295
	1.68	850	550	460
	0.84	1,500	900	740
	0.42	2,600	1,600	1,400
	0.168	6,000	3,500	2,600
	0.084	11,000	5,400	5,200
500	16.8	167	113	109
	8.4	246	170	158
	3.36	495	265	295
	1.68	830	510	450
	0.84	1,460	960	760
	0.42	2,720	1,520	1,360
	0.168	6,200	3,500	2,800
	0.084	11,000	4,600	4,000

Table B-12

PROPERTIES OF VACUUM TOWER BOTTOMS

Period, P99-	SP. GR. 77/77F	Melting Pt., °F	Pyridine Insol, Wt%	Ash, Wt%	Elemental Analysis, Wt %				
					C	H	N	O	S
54-4	1.494	280	34.79	22.00	69.95	4.19	1.36		1.88
54-5	1.420	302	37.94	22.90	69.47	4.05	1.40	11.1	1.92
54-8	1.438	316	38.03	21.68	69.36	3.99	1.43	12.0	1.89
54-9	1.460	347	39.13	21.83					
54-11	1.476	325	37.60	21.92	69.10	3.96	1.42	11.3	2.09
54-12A	1.479	329	39.95	23.21	67.44	3.81	1.41	12.1	2.12
54-12B	1.496	347	39.88	23.05	68.64	3.87	1.43	13.7	2.01
55-0	1.450	329	38.19	22.26	69.26	3.99	1.45	12.6	2.04
55-1	1.448	329	37.40	21.32	69.85	3.84	1.45	11.3	2.01
55-2	1.468	338	40.75	23.23	68.62	3.85	1.42	15.2	2.00
55-3	1.473	338	40.66	21.43	68.64	4.00	1.42	13.0	1.99
55-4	1.480	320	40.97	22.66	69.10	4.11	1.41	12.4	1.99
55-5A	1.467	329	42.30	23.75	67.87	3.80	1.39	12.9	2.03
55-5B	1.460	320	42.46	23.78	67.47	3.70	1.38	13.1	2.03
55-6	1.452	325	41.10	23.14	68.23	3.71	1.40	13.0	2.04
55-7	1.453	320	43.22	23.68	68.60	4.01	1.41	12.4	2.02

Table B-13

EMISSION SPECTROGRAPHIC ANALYSIS OF FRACTIONATOR BOTTOMS

Run No., P99-	54-4	54-5	54-8	54-11	54-12A	54-12B	55-0	55-1	55-2	55-3	55-4	55-5	55-6	55-7
Metals Analyses, ppm														
Aluminum	0.06	0.09	0.05	0.12	0.1	0.04	0.1	0.05	0.4	0.04	0.1	0.09	0.09	0.1
Barium	tr	tr	0.3	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr
Boron	0.6	0.5	0.08	0.32	0.07	0.3	0.03	0.1	0.7	0.1	0.06	0.04	0.2	0.5
Calcium	—	—	—	—	0.02	0.01	tr	0.06	—	—	0.03	0.01	—	—
Chromium	1	0.8	0.6	1.2	2	2	0.2	0.8	8	1	0.6	0.8	2	3
Cobalt	—	0.05	0.009	0.08	0.07	0.004	0.01	—	—	—	—	—	—	—
Copper	0.008	0.02	0.005	0.20	0.02	0.005	0.006	0.004	0.03	0.004	0.004	0.009	0.01	0.02
Iron	6	20	2	20	9	3	6	4	30	4	2	4	9	15
Lead	0.02	—	0.01	—	0.04	0.04	0.02	0.03	—	—	0.05	—	—	—
Magnesium	0.006	0.005	0.003	0.008	0.06	0.005	0.006	0.008	5	0.005	0.05	0.006	0.005	1
Manganese	0.6	0.2	0.2	0.28	0.3	0.3	0.3	0.2	1	0.2	0.1	0.2	0.6	0.6
Molybdenum	0.06	0.2	0.08	0.24	0.1	0.03	0.04	0.04	0.3	0.03	0.03	0.08	0.08	0.1
Nickel	0.1	1	0.5	2	1	0.4	0.1	0.3	2	0.2	0.08	0.9	0.7	1
Potassium	0.005	0.005	0.01	0.01	0.02	0.009	0.006	0.008	0.005	0.003	0.007	0.03	0.006	0.006
Phosphorus	0.2	0.5	—	—	—	—	—	—	—	—	—	—	—	—
Silicon	0.1	0.2	0.3	0.16	0.3	0.2	0.3	0.3	2	0.2	3	0.3	0.3	0.2
Sodium	0.01	0.05	0.03	0.02	0.09	0.06	0.06	0.06	0.04	0.05	0.04	0.1	0.06	0.08
Strontium	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Tin	0.1	0.05	0.08	0.12	0.2	0.1	0.04	0.07	0.9	0.1	0.05	0.09	0.1	0.2
Titanium	0.008	0.008	0.005	—	0.02	0.008	0.008	0.004	0.06	0.006	0.008	0.01	0.007	0.01
Vanadium	—	—	—	—	—	—	—	tr	tr	—	—	—	—	—

Table B-14

EMISSION SPECTROGRAPHIC ANALYSIS OF VACUUM TOWER OVERHEAD

Run No., P99-	54-4	54-5	54-11	54-12A	54-12B	55-0	55-1	55-2	55-3	55-4	55-5	55-6	55-7
Metals Analyses, ppm													
Aluminum	0.7	0.05	0.7	0.2	0.8	0.4	0.09	1	0.1	0.2	0.2	0.3	0.2
Barium	tr	0.1	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr	tr
Boron	0.05	0.03	0.07	0.1	0.2	0.04	0.4	0.06	0.03	0.05	0.03	0.04	0.05
Calcium	0.06	0.008	0.035	0.01	0.08	0.04	0.002	0.09	0.01	0.03	0.01	0.03	0.01
Chromium	0.004	0.01	0.02	0.02	0.03	0.003	0.005	0.007	0.002	0.02	0.008	0.002	0.01
Cobalt	--	--	--	0.003	--	--	--	--	--	--	--	--	--
Copper	0.003	0.005	0.003	0.0006	0.3	0.003	0.002	0.006	0.001	0.001	0.0004	0.002	0.0005
Iron	0.8	0.08	1	0.4	0.4	0.4	0.08	1	0.1	0.2	0.2	0.3	0.09
Lead	0.02	0.005	0.042	0.02	0.1	0.01	2	0.05	0.01	0.02	--	0.02	0.01
Magnesium	0.1	0.01	0.14	0.009	0.1	0.06	0.008	0.1	0.01	0.04	0.03	0.04	0.02
Manganese	0.008	--	0.021	0.004	0.03	0.004	0.01	0.02	0.002	0.007	0.002	0.006	0.003
Molybdenum	--	0.003	0.007	0.002	0.007	0.002	--	--	0.002	0.002	0.002	0.003	0.002
Nickel	0.006	0.005	--	0.01	0.05	0.008	0.02	0.01	0.004	0.02	0.006	0.009	0.005
Potassium	0.05	*	0.1	--	*	0.02	0.02	0.1	*	--	*	*	*
Phosphorus	0.06	0.005	--	--	--	--	--	--	--	0.04	--	--	--
Silicon	1	0.3	1	0.9	3	0.7	3	2	0.6	0.5	0.8	1	0.6
Sodium	0.02	*	0.06	--	*	0.2	0.07	0.5	*	--	*	*	*
Strontium	0.005	--	--	0.001	0.006	0.002	--	0.006	0.008	0.002	0.0007	0.003	0.001
Tin	0.02	0.003	0.03	--	0.1	0.007	--	--	0.003	0.01	0.01	0.006	0.006
Titanium	0.05	0.006	0.07	0.02	0.08	0.03	0.01	0.1	0.01	0.03	0.01	0.05	0.02
Vanadium	--	--	0.014	--	0.03	--	--	--	0.001	--	--	tr	0.002
Zinc	0.07	--	--	--	0.6	0.04	--	--	--	0.02	--	--	--

* Insufficient ash for Na or K determination.

FIGURE B-1
P-99 VACUUM COLUMN

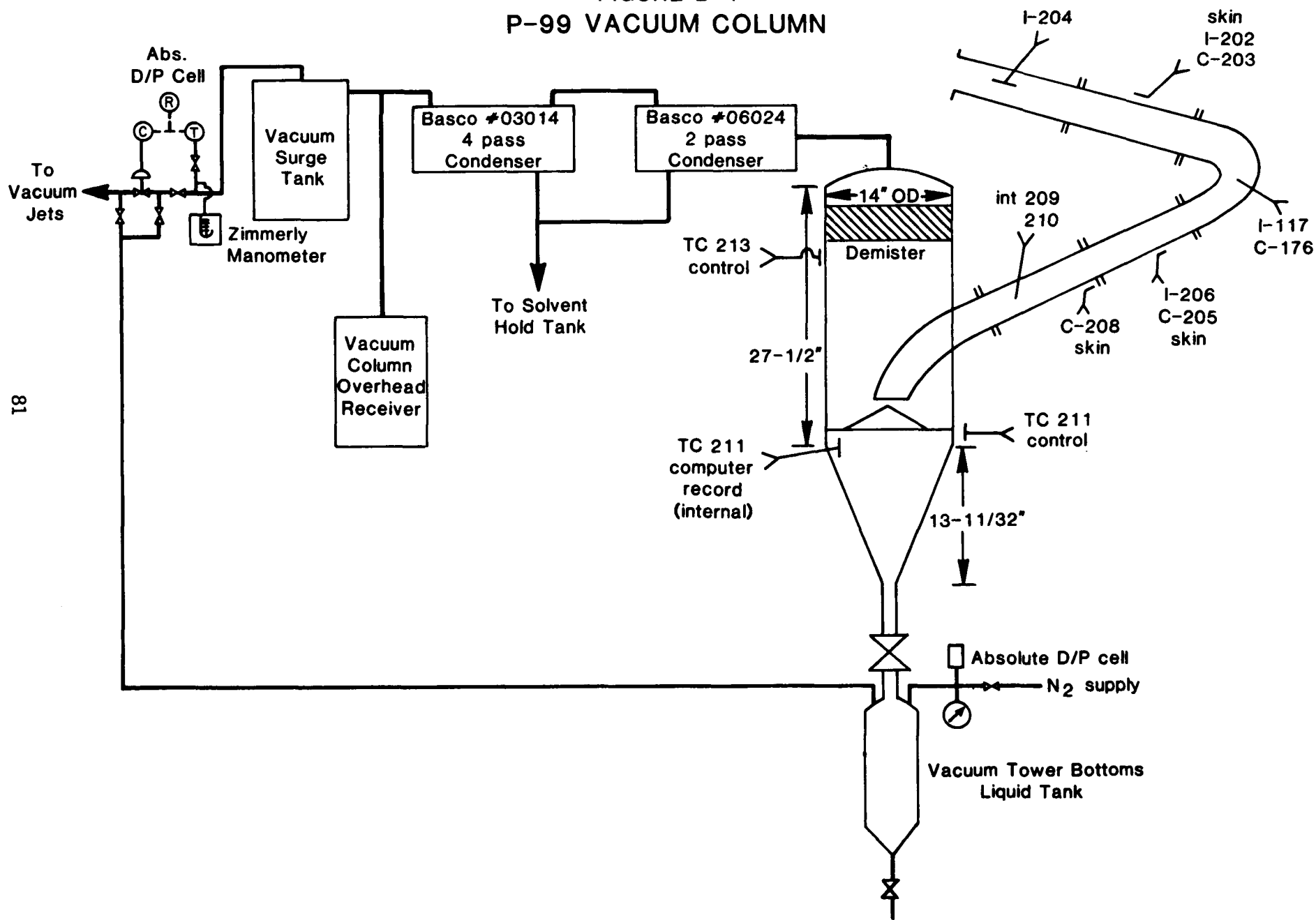


FIGURE B-2
VISCOSITY VS. 1/T (ABSOLUTE)

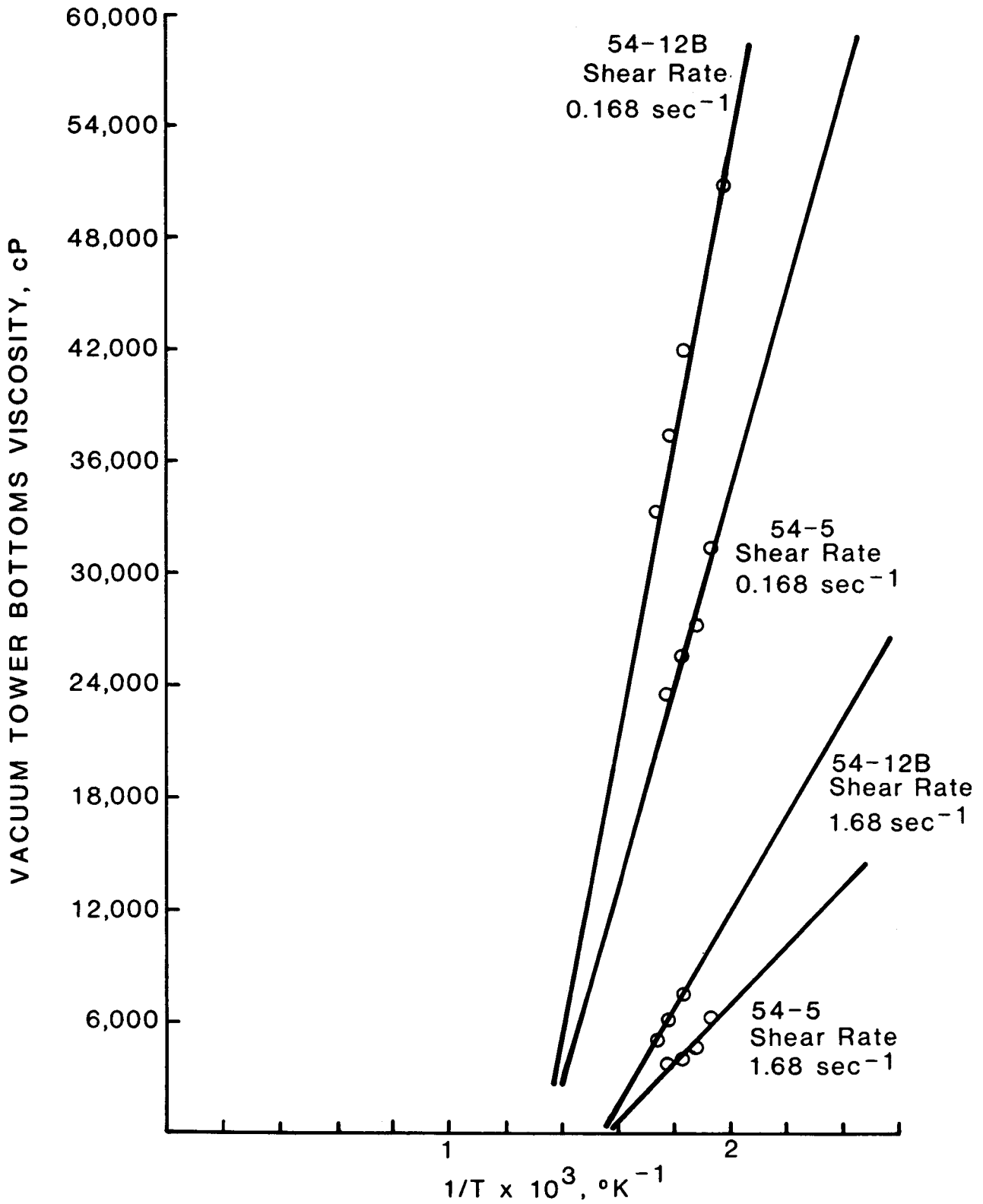


FIGURE B-3
VTB VISCOSITY VS. FLASH ZONE TEMPERATURE

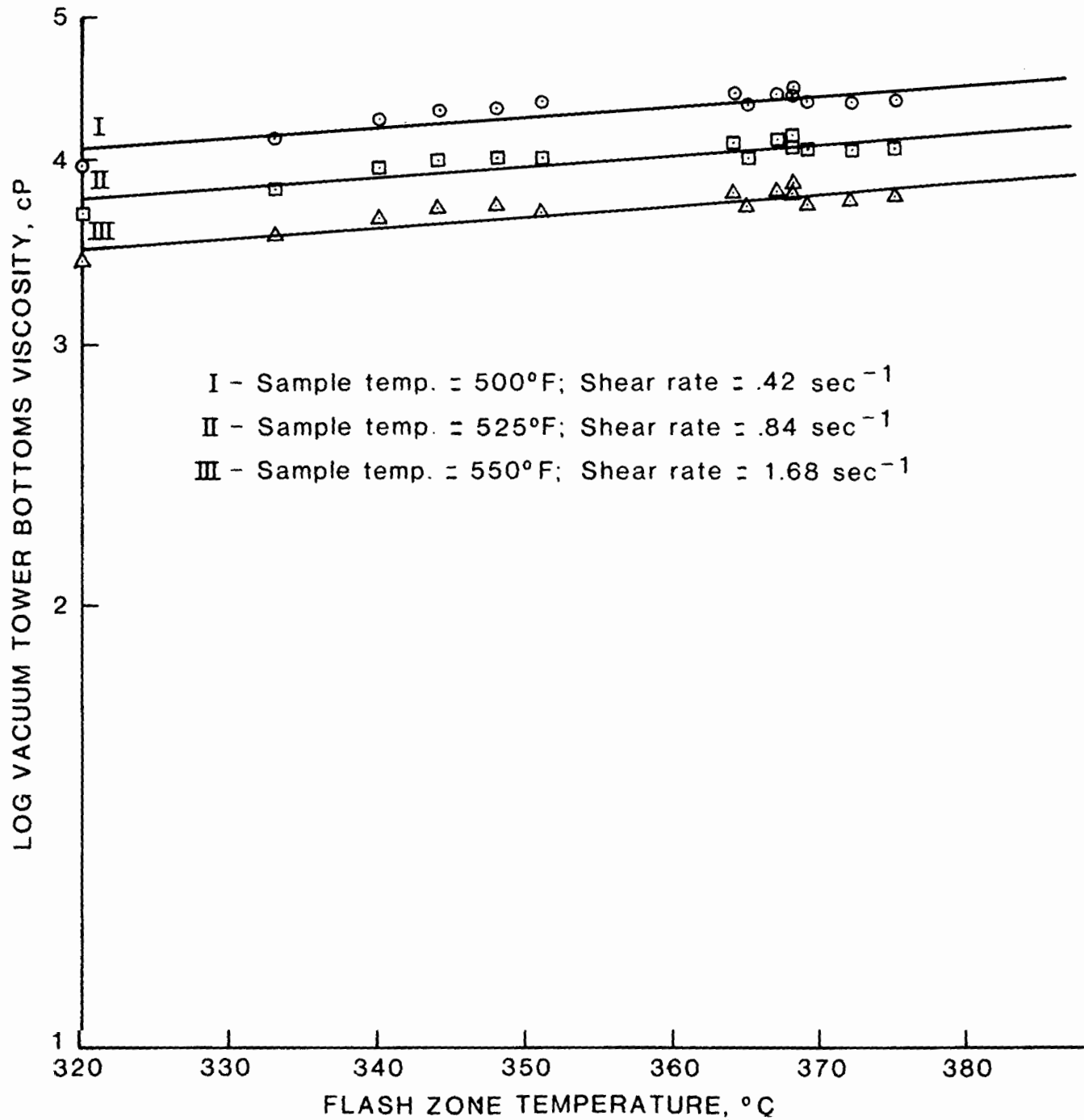


FIGURE B-4

FLASH ZONE TEMPERATURE VS. % DISTILLATE IN VTB

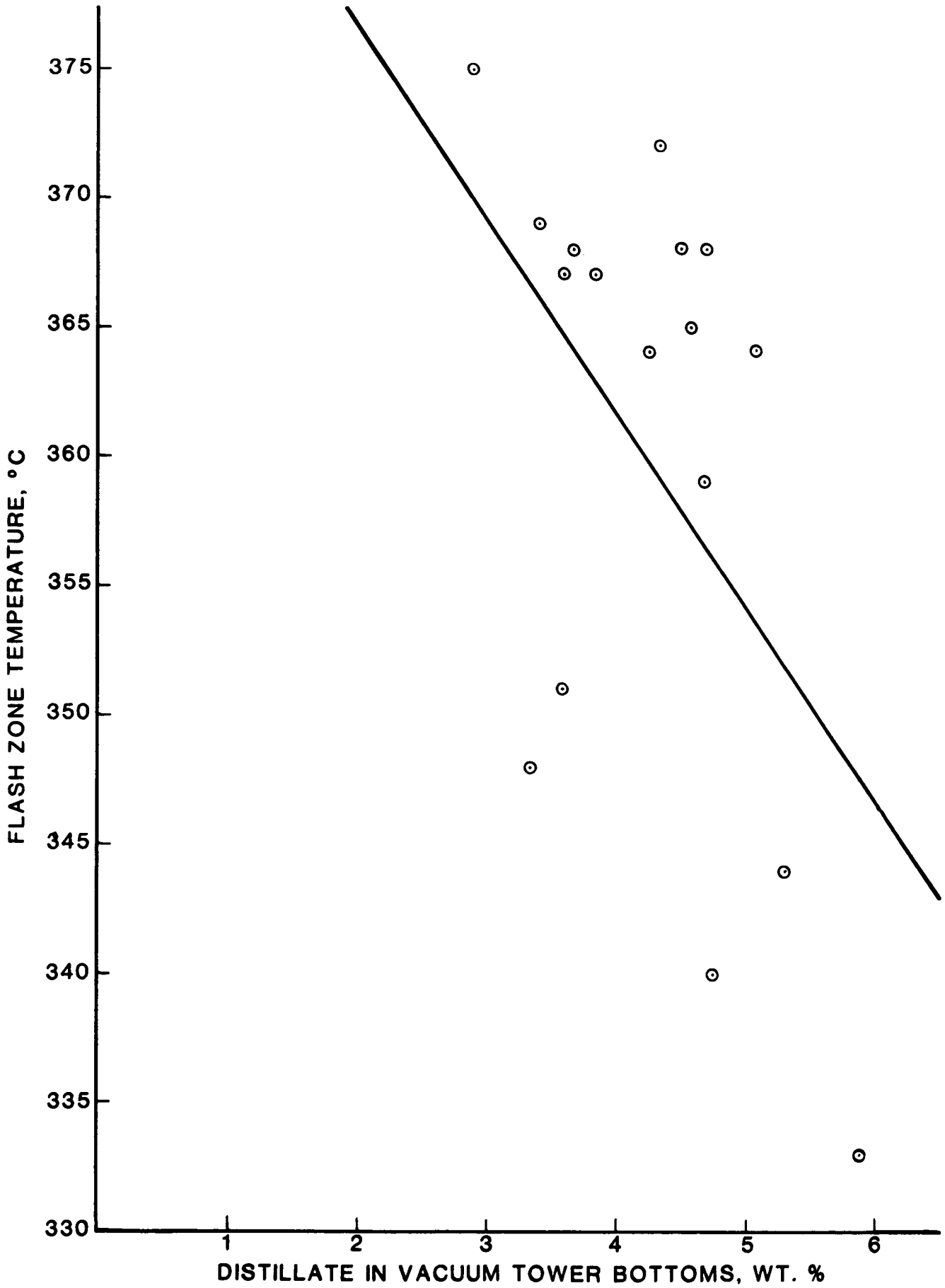


FIGURE B-5

VTB VISCOSITY VS. % DISTILLATE IN VTB

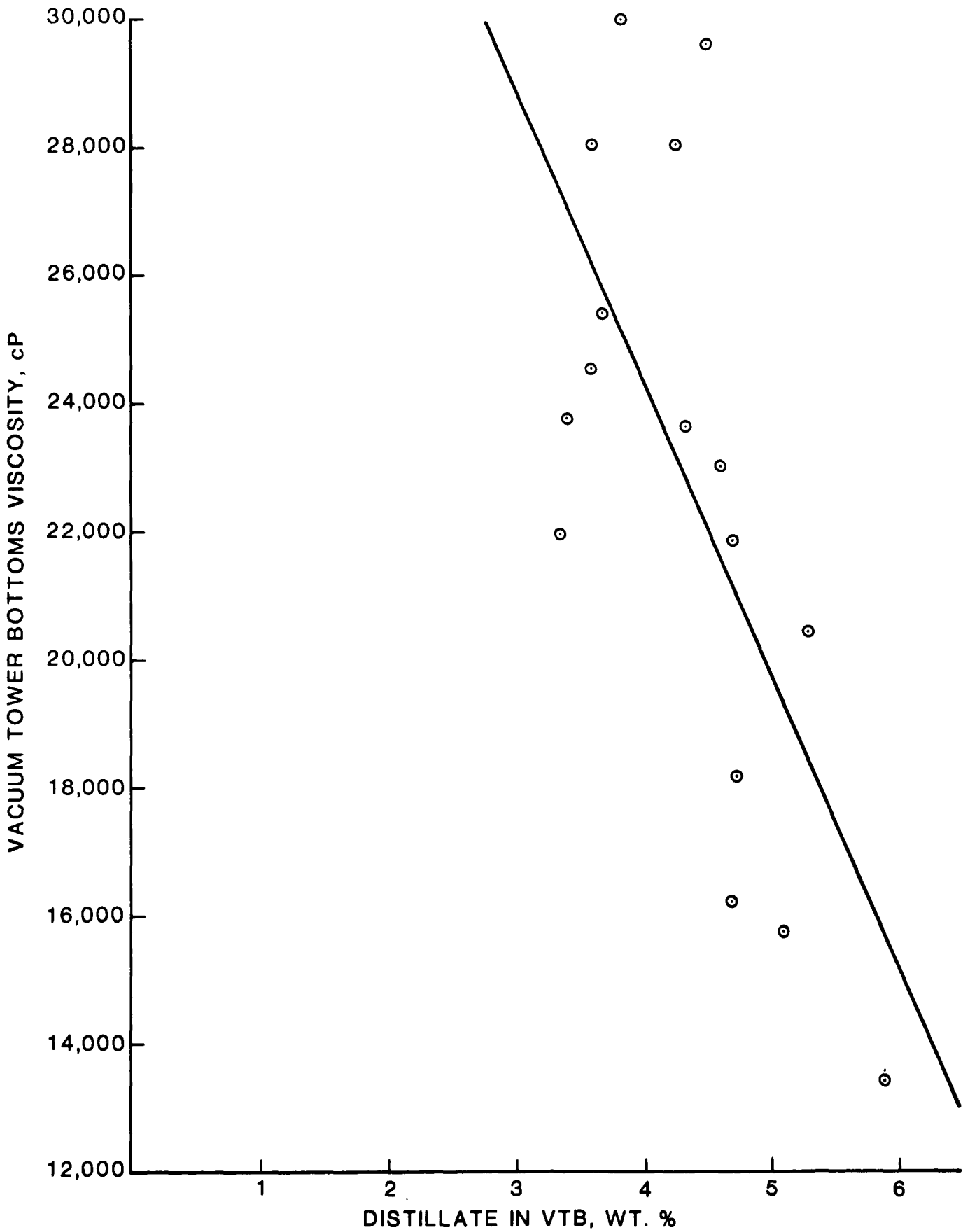


FIGURE B-6

VACUUM COLUMN FEED DISTILLATION
CURVE FOR PERIOD P99-54-11

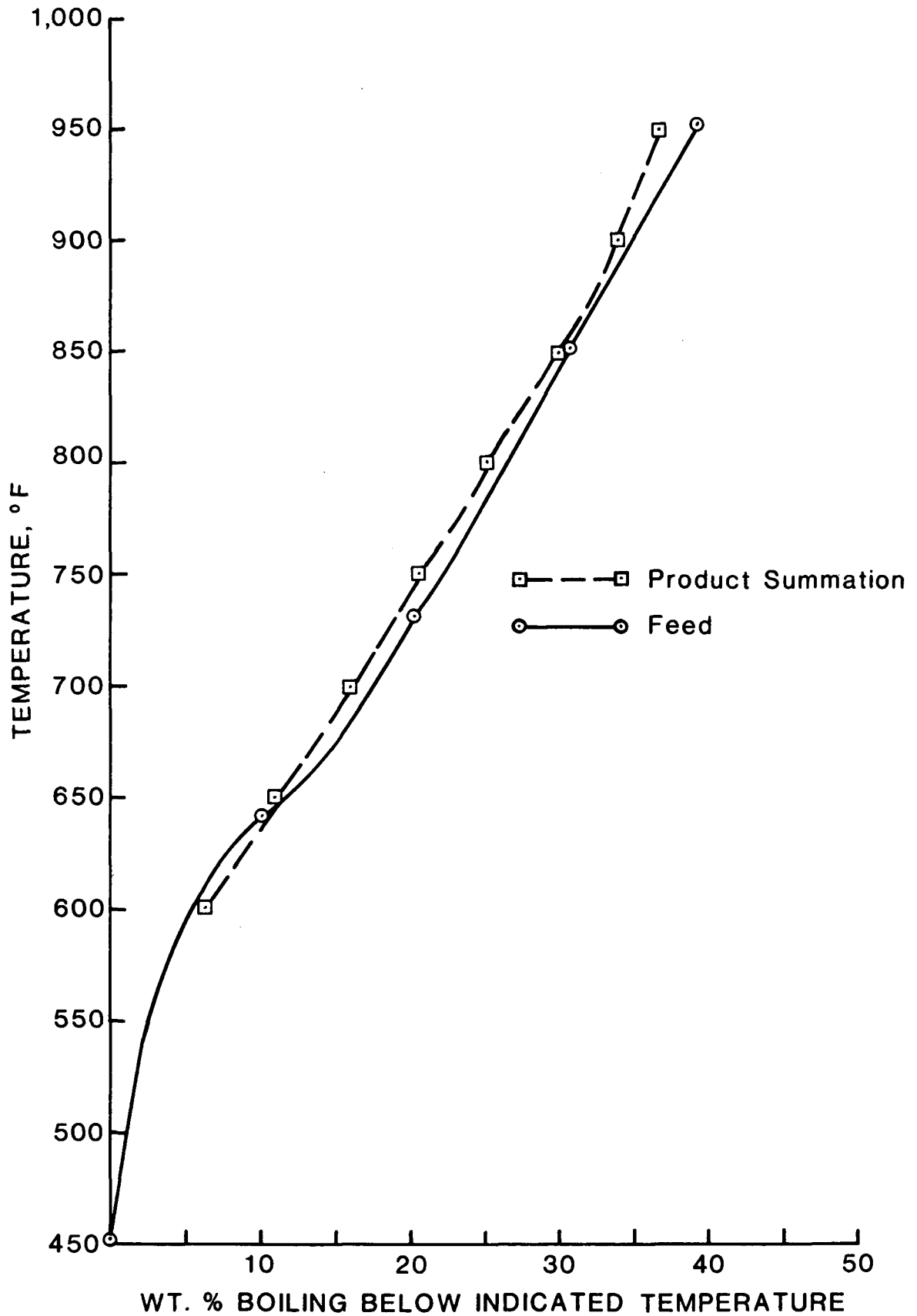


FIGURE B-7

VACUUM COLUMN FEED DISTILLATION
CURVE FOR PERIOD P99-54-12A

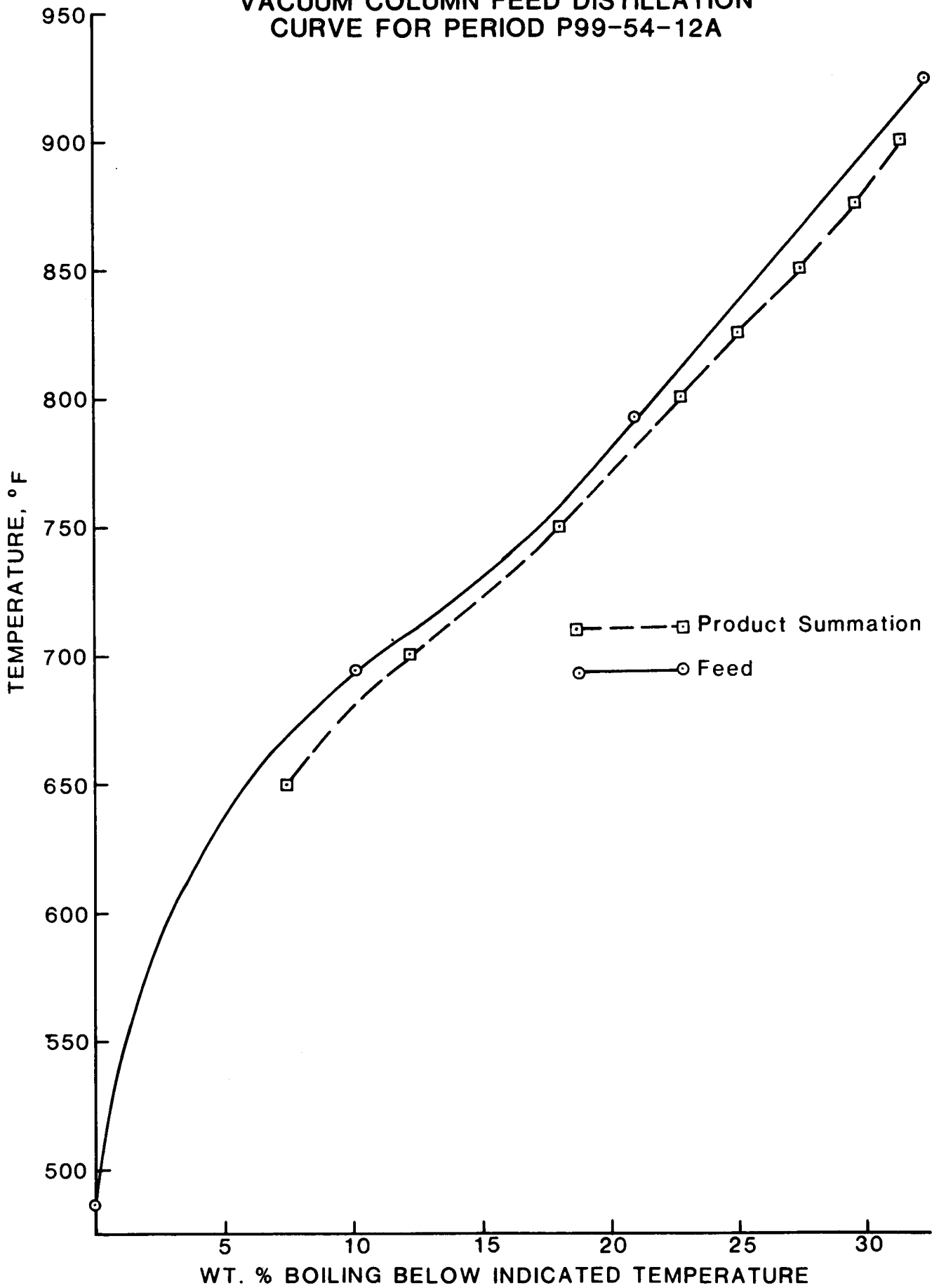
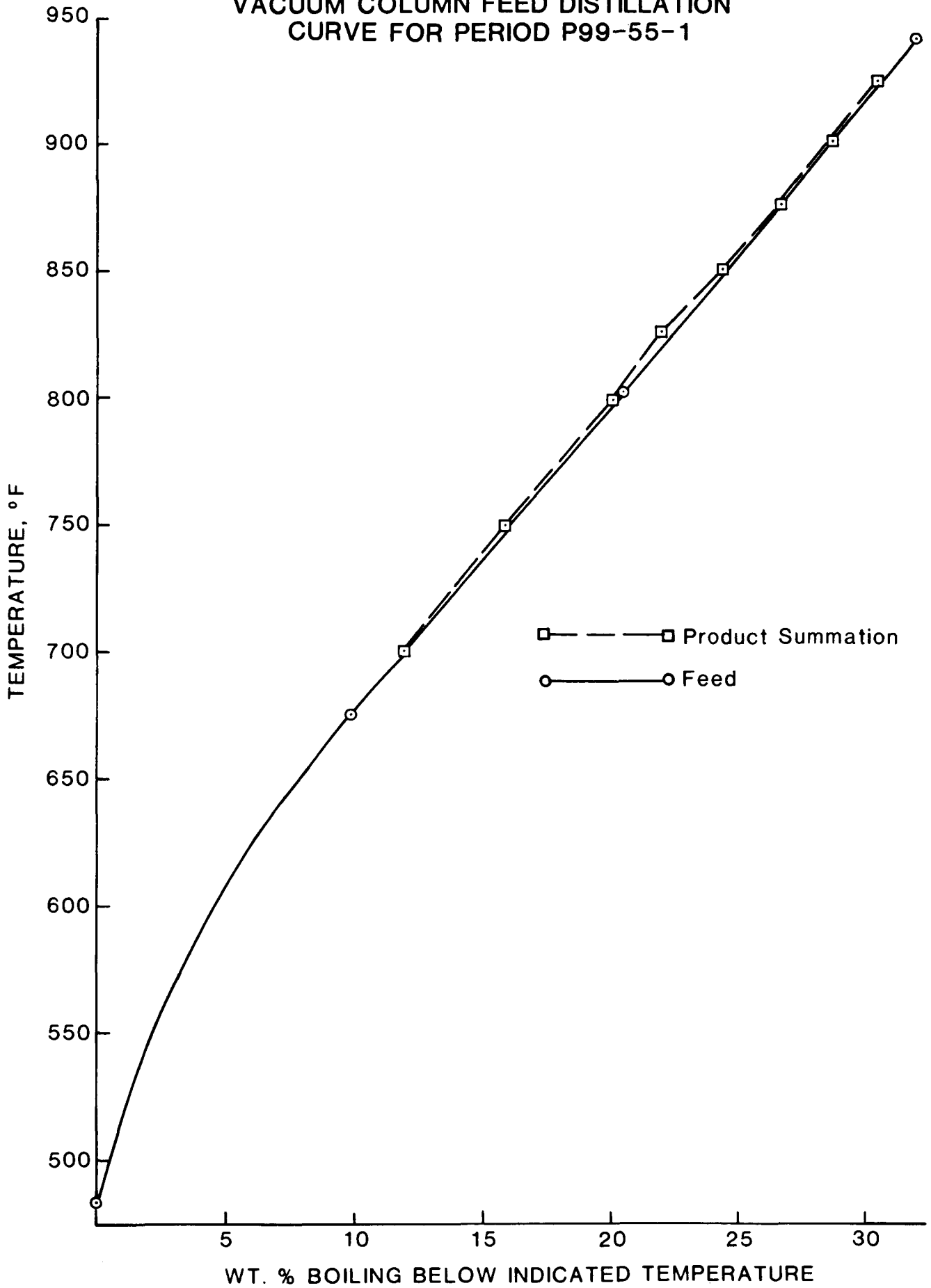


FIGURE B-8
VACUUM COLUMN FEED DISTILLATION
CURVE FOR PERIOD P99-55-1



A P P E N D I X C
CHEMICAL ANALYSIS AND LEACHING OF COAL
CONVERSION SOLID WASTES

CHEMICAL ANALYSIS AND LEACHING OF COAL
CONVERSION SOLID WASTES

by

R. A. Griffin, R. M. Schuller, S. J. Russell, and N. F. Shimp

Illinois State Geological Survey
University of Illinois
Urbana, Illinois 61801

Paper for presentation at the Research Symposium, Environmental Aspects of Fuel Conversion Technology IV, April 17-20, 1979 at Hollywood, Florida. Sponsored by U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

CHEMICAL ANALYSIS AND LEACHING OF COAL
CONVERSION SOLID WASTES

by

R. A. Griffin, R. M. Schuller, S. J. Russell,
and N. F. Shimp

Illinois State Geological Survey
Urbana, Illinois 61801

ABSTRACT

Five solid wastes from coal conversion processes were characterized chemically and mineralogically. The wastes included three Lurgi gasification ashes and mineral residues from the SRC-I and H-Coal liquefaction processes. Chemical analyses of the solid wastes were performed for 60 constituents. Mineralogical characterization of the solid wastes was carried out using X-ray diffraction, Mössbauer spectroscopy, scanning electron microscopy, and optical techniques.

Leachates generated from the solid wastes at eight pH levels and under two different gas atmospheres were analyzed for over 40 chemical constituents. Thermodynamic speciation of inorganic ions and complexes in solution were modeled. There were 115 aqueous species considered in the model, and saturation data were computed for over 100 minerals.

Results of the mineralogical characterization and leachate analyses showed a wide range in constituent concentration and in the minerals present in the solid wastes. However, thermochemical modeling demonstrated that similar mineral phases controlled the aqueous solubility of the major ionic species for all five solid wastes.

CHEMICAL ANALYSIS AND LEACHING OF COAL CONVERSION SOLID WASTES

INTRODUCTION

Although the fuels produced by coal gasification and liquefaction processes are free of certain pollution hazards, e.g. sulfur, accessory elements from the coal may be present in them or especially concentrated in the waste streams. These waste products will have to be characterized before environmentally acceptable methods for their disposal can be developed.

Until recently, the main emphasis has been on the characterization of airborne contaminants from coal conversion processes. However, several investigators, including Cavanaugh and Thomas¹, Cavanaugh et al.², and Somerville and Elder³, have recently characterized the waste streams from low/medium BTU gasifiers. Filby et al.⁴, has characterized the trace elements in the solid wastes from the SRC-I liquefaction process. These waste characterizations are important, as was demonstrated by the work of Sinor⁵, who determined that the flow rate of Ni, As, Cd, and Pb from a Lurgi gasification plant may be environmentally significant. Due to the large quantities of raw materials consumed, there is a potential for discharge of accessory elements which may be hazardous, even though they may be present in the waste in only very low concentrations.

Because the quantity of solid wastes produced from coal conversion processes can be very large and variable (Griffin et al.⁶), detailed characterization of the wastes is justified and, indeed, necessary. However, characterization alone is insufficient for the evaluation of acceptable disposal methods for the wastes. Therefore it is necessary to determine which elements can be leached from the wastes and under what circumstances.

The solubility of the accessory elements in coal conversion ashes and residues has not been thoroughly investigated. Some gasification ashes and liquefaction residues are produced under relatively severe conditions, namely, at high temperatures and/or pressures. Liquefaction residues are produced under a reducing atmosphere. Such conditions can alter the mineralogy and subsequent solubility of accessory elements in the feed coals and can thus affect their potential release of pollutants.

The application of equilibrium solubility models can lead to useful insights into the chemistry of aqueous systems. Equilibrium models provide, at a minimum, boundary conditions within which questions may be framed. For example, a typical environmental problem solved by equilibrium models is that of predicting the highest concentration of a given constituent that can be achieved in solution before precipitation occurs with a given solid phase. Solutions to such problems can be useful in developing a "worst case" scenario for a given pollutant leaching from a solid waste by setting the upper boundary for concentrations of the pollutant that will have to be dealt with under a given set of conditions.

Applications of solubility models to environmental problems must be interpreted with care. For example, it is not uncommon to find large discrepancies in literature values for the solubility products of some mineral phases. The value of the solubility product may depend on the direction of approach to equilibrium, using well defined crystals versus precipitation, and phenomena such

as phase transitions, aging, colloid formation and differences in particle size. These factors, along with slow attainment of equilibrium and the fact that impure minerals are found in nature as opposed to the pure minerals used to determine solubility constants, may obscure solubility relationships and their application to practical environmental problems.

Important factors controlling the solubility of mineral phases include pH, redox environment of the system, oxidation state of the mineral components, concentration and speciation of individual inorganic and organic ions and complexes in solution, and ionic strength (total soluble ions). Application of results from solubility models to real environmental conditions requires considerable caution. Nevertheless, assuming that the activities are calculated correctly and that the equilibrium constants are numerically factual, the models should accurately predict the solubility of an ion under a given set of conditions for an exhaustive list of solid phases.

Purpose

The purpose of this study was to investigate the potential pollution hazards of selected coal conversion solid wastes. The project is part of an ongoing research effort by the Illinois State Geological Survey into the characterization of coal and coal residues (Ruch et al.⁷; Ruch et al.⁸; Ruch et al.⁹; Gluskoter¹⁰, and Gluskoter et al.¹¹). The five wastes chosen for this study included

(1) three Lurgi gasification ashes from runs employing three different feed coals and (2) two liquefaction residues, an SRC-I dry mineral residue and an H-Coal vacuum still bottoms mineral residue. It is beyond the scope of this study to give a description of the three coal conversion process technologies, but these are available elsewhere (e.g., Braunstein et al.¹²; and Parker and Dykstra¹³).

To assess the solubility of the accessory elements contained in the solid wastes, this study was developed in four stages:

- (1) chemical characterization of the solid wastes,
- (2) mineralogical characterization of the solid wastes,
- (3) determination of the soluble constituents from the solid wastes, and
- (4) application of thermochemical equilibrium modeling to determine the mineral phases controlling the solubilities of accessory elements in the solid wastes.

CURRENT STUDIES OF THE SOLUBILITY OF COAL GASIFICATION AND LIQUEFACTION SOLID WASTES

Sources of Gasification Ashes and Liquefaction Residues

During 1973 and 1974, the American Gas Association and the Office of Coal Research studied the performance and suitability of various American coals for gasification by the Lurgi process. Four different coals were sent to Scotland, where they were gasified in the Lurgi plant at Westfield. Among these four coals were 5000 tons each of Illinois No. 6 and No. 5 (seam) coals and a Rosebud (seam) coal from Montana that was gasified. The unquenched waste ash was then sent back to the United States and has since been used in several studies. The samples of Illinois No. 5, No. 6, and Rosebud Lurgi ash, for which data are reported here, were supplied to us by Peabody Coal Company's Central Laboratory at Freeburg, Illinois.

The H-Coal liquefaction residue was obtained from Hydrocarbon Research, Inc., Trenton, New Jersey. The residue was the vacuum still bottoms generated during production of a fuel oil product using an Illinois No. 6 (seam) coal and the H-Coal^R pilot development unit at the HRI Trenton Lab on May 3, 1976.

The SRC-I liquefaction dry mineral residue was obtained in September 1976 from the Pittsburg and Midway Coal Mining Co. solvent refined coal pilot plant at Fort Lewis, Washington. A Kentucky No. 9 (seam) coal was being processed at the time the sample was obtained.

Chemical Characterization

The chemical composition of the five solid wastes have been characterized for over 60 chemical constituents including major, minor, trace, and rare earth elements using the methods described by Gluskoter et al.¹¹. The results of these analyses have been reported previously by Griffin et al.⁶, Schuller et al.¹⁴, and Griffin et al.¹⁵. To summarize, nine elements were generally found in concentrations greater than 1000 mg/kg of the solid wastes. These were Al, Ca, Fe, K, Mg, Na, S, Si, and Ti. An additional group of elements was found in concentrations generally between 100 mg/kg and 1000 mg/kg. These included B, Ba, Ce, Cl, Cr, F, Mn, Sr, V, Zn, and Zr. Another 20 elements were found in detectable concentrations less than 100 mg/kg.

The most noteworthy differences in chemical composition between the wastes were the high levels of Ca and Mn in the ashes from the Lurgi process and the high levels of S and Cl in the two liquefaction residues. The wastes from the Rosebud and Kentucky No. 9 coals contained higher levels of P and F than did the wastes from the Illinois Coals. Trace element composition was highly variable, and no clear pattern could be distinguished. Zn concentrations varied over the widest range (13 to 1500 ppm), presumably in response to the presence or absence of ZnS in the feed coals. Correlation between the chemical characterization of the wastes from this study and other investigations is quite difficult. The difficulty arises from the variability within the feed coals employed and the process parameters used. Changes in temperatures and pressures will affect the fate of constituents and the nature of the various coal conversion process waste streams.

Mineralogical Characterization

Samples of the five solid wastes were analyzed by X-ray diffraction, Mössbauer spectroscopy, scanning electron microscopy, and optical techniques. The minerals identified are listed in Table 1. Comparison of the mineralogy of the samples from the gasification and liquefaction processes is instructive from the standpoint of the mineral transformations occurring during coal conversion. For example, pyrite (FeS₂) is the dominant form of iron in the feed coals but is not detected in any of the solid wastes. The pyrite has been converted to hematite and magnetite during the Lurgi gasification process. In contrast, the pyrite has been converted to pyrrhotite and troilite during the liquefaction processes. Another interesting contrast occurs in the clay minerals present in the feed coals. They remain unaltered during the liquefaction processes, but are converted to feldspar and mullite during the Lurgi gasification process.

Table 1. Minerals identified in coal conversion solid wastes.

Minerals Identified	Lurgi IL 5	Lurgi IL 6	Lurgi Rose-bud	H-Coal IL 6	SRC KY 9
Hematite (Fe ₂ O ₃)	X	X	X		
Magnetite (Fe ₃ O ₄)	X	X	X		
Goethite (FeOOH)	X	X	X		
Pyrrhotite (Fe _{1-x} S)				X	X
Troilite (FeS)				X	X
Sphalerite (ZnS)				X	
Quartz (SiO ₂)	X	X	X	X	X
Gypsum-Anhydrite (CaSO ₄)	X	X	X		X
Calcite-Dolomite (CaCO ₃ -CaMg(CO ₃) ₂)			X	X	
Wollastonite (CaSiO ₃)				X	
Plagioclase Feldspar Na(Ca)AlSi ₃ O ₈	X	X	X		
Mullite (3Al ₂ O ₃ ·2SiO ₂)	X	X	X		
Clay Minerals				X	X

Aqueous Solubility

To determine the soluble constituents of the five solid wastes, large volume, static leaching tests were used. This involved the making of 10 percent (weight to volume) slurries of solid waste with distilled water in large glass carboys. The slurries were made in a series of four and adjusted to pH values over the range 2 to 11. The pH values of the slurries were monitored and readjusted to the specified values when necessary. Chemical equilibrium was assumed when the pH remained constant. The period for achieving equilibrium lasted 3 to 6 months. However, studies conducted with the Lurgi ashes indicated that they had reached over 90 percent of their equilibrium concentrations within one week. Duplicate sets of the slurries were made; one set was equilibrated under an argon (oxygen- and CO₂-free) atmosphere and the other under an air atmosphere.

The leachates from the wastes were analyzed for 43 constituents, and these concentrations were compared to recommended water quality levels (US-EPA¹⁶). The results of the actual leachate analyses have been reported previously by Griffin et al.⁶ and Griffin et al.¹⁵. Table 2 lists those constituents found to exceed the recommended levels over the pH range studied and under the laboratory conditions described above. Although many constituents exceed the recommended levels under acid conditions, those that exceed the recommended levels over the entire pH range or at their natural pH were felt to represent the highest potential for pollution. These constituents are listed under the "Natural pH" column in Table 2. Also given in Table 2 are the pH ranges of the leachates used and the pH values of the two natural pH solutions for each aerobic (air) and anerobic (argon) set of slurries for each waste. The natural pH slurries are those that were allowed to equilibrate without pH adjustment by addition of either nitric acid or sodium hydroxide. Table 2 indicates that there is a strong similarity between the soluble constituents found in a solid waste and the treatment that it undergoes, i.e., the three Lurgi ashes yielded nearly the same major soluble constituents for all three feed coals employed. The same was true for the two liquefaction wastes. The Illinois No. 6 coal was used in both the Lurgi and H-Coal processes but resulted in the derivation of quite different soluble constituents from their wastes. The levels of Cd, K, Mn, Na, Pb, and Sb found in the Lurgi ash leachates were higher than those found in the leachates from the H-Coal and SRC residues under the conditions employed.

Table 2. Constituents with concentrations exceeding recommended water quality levels under the laboratory test conditions.

Sample	Natural pH		Constituents	Adjusted pH	
	Air	Argon		Range	Additional constituents leached
Lurgi Ash Illinois #6 Coal	7.6	8.9	B, Ca, Cd, K, Mn, NH ₄ , Pb, SO ₄ , Sb	8.9-2.7	Al, Cr, Co, Cu, Fe, Zn
Lurgi Ash Illinois #5 Coal	8.3	10.9	B, Ca, K, Mn, NH ₄ , Pb, SO ₄ , Sb	10.9-3.1	Al, Cd, Cr, Co, Cu, Fe, Ni, Zn
Lurgi Ash Rosebud Coal	8.5	11.1	B, Ca, Cd, F, K, Mo, NH ₄ , Pb, SO ₄ , Sb	11.1-3.1	Al, Cr, Co, Cu, Fe, Mg, Mn, P, Zn
SRC-I Kentucky #9 Coal	6.4	7.5	B, Ca, Fe, Mn, NH ₄ , SO ₄	10.2-2.9	Al, Be, Cd, Cr, Co, K, Ni, Pb, P, V, Zn
H-Coal Illinois #6 Coal	8.8	11.3	Al, B, Ca, NH ₄	11.3-2.3	F, Fe, Mn, Pb, Zn

In addition to those constituents listed under the "Natural pH" column in Table 2, Al, Be, Cr, Co, Cu, F, Fe, Mg, Ni, P, V, and Zn were found in the leachates at concentration levels exceeding the recommended levels in water under certain pH conditions, generally when the pH was quite acid. Discharges of the constituents listed in Table 2 at the levels found in this study could cause some environmental degradation and require some form of waste water treatment.

Equilibrium Solubility Model

It is difficult to explain the aqueous chemistry of a complex system such as the leachates from coal conversion solid wastes. Possible complexation, ion pair formation, and the effects of organic components on the formation of organo-metallic complexes hinders the description of these systems. On the other hand, it is still of interest to examine these systems in an effort to account for their soluble components, and we progress if we prepare diagrams showing the relations of the known aqueous species to the mineral solid phases.

The solubility and mineral stability diagrams were prepared as described by Garrels and Christ¹⁷. The thermodynamic solubility model used in this study (WATEQF) considered the speciation of 115 aqueous inorganic ions and complexes and computed saturation data for over 100 minerals. The theory of the model and its computer implementation have been discussed previously by Truesdell and Jones^{18,19} and Plummer, Jones, and Truesdell²⁰.

The stability relations of the iron oxides and sulfides in water are shown in Figure 1 plotted as a function of Eh and pH. The data from the leachates of the five wastes and a pyrite standard, equilibrated under the same conditions as the solid wastes, are shown plotted on the diagram.

Some explanation of the diagram may aid in interpretation of the data. The upper and lower limits of water stability are shown on the diagram and mark the upper and lower boundaries of Eh and pH of concern. That is, at Eh and pH values above the upper boundary shown, water decomposes into oxygen gas and likewise at the lower boundary decomposes into hydrogen gas. Thus, Eh and pH values outside this range are not normally of concern when interpreting the aqueous chemistry of natural systems.

The solid lines between solid phases such as hematite and magnetite mark the boundaries of mineral stabilities. Data points falling within these regions indicate that the samples are within the stability field of the particular mineral. Most of the data points shown in Figure 1 fall within the hematite stability field. This is reasonable since hematite was identified by X-ray diffraction as being present in most of the samples. However, magnetite and pyrrhotite were also identified as minerals present in the solid wastes. These diagrams illustrate that these two minerals are unstable in these systems and, given sufficient time, will decompose to other mineral phases.

Data points that fall on or near a boundary line, such as the pyrite standard plotted in Figure 1, illustrate a solution in simultaneous equilibrium with the various solid phases described by the boundary. The pyrite used in this study was a technical grade material that contained both hematite and magnetite as impurities; thus it is reasonable that the solution would be in equilibrium with these three mineral phases and serves to illustrate that the electrodes used in the measurements were operating properly.

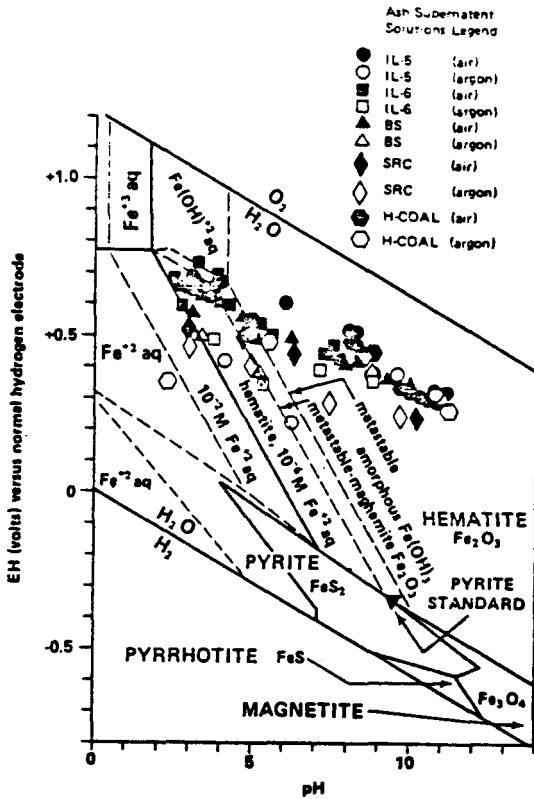


Figure 1. Stability relations of iron oxides and sulfides in water at 25°C when the sum of S = 10^{-3} M and $Fe^{+2}_{aq} = 10^{-6}$ M.

The boundaries between solid phases and aqueous species such as between hematite and the aqueous Fe^{+2} ion serve as true "solubility" boundaries; as such they are a function of the activity of the ion in solution. Two boundaries are shown in Figure 1, one for 10^{-6} M and another for 10^{-2} M Fe^{+2}_{aq} . The 10^{-6} M boundary is chosen by convention, on the premise that if the activity of an ion in equilibrium with a solid phase is less than 10^{-6} M the solid will be immobile in the particular environment. This convention was developed largely from experience but seems to correlate well with natural geologic systems. The 10^{-6} M boundary was chosen because it corresponds to the upper limit of Fe^{+2} concentrations measured in the leachates from the solid wastes.

The boundary between two aqueous species such as Fe^{+2} and Fe^{+3} ion is drawn where the concentration of each ion is equal. Thus, the labeled areas are those where the particular ion is the dominant one but small concentrations of other ions may also be present.

The 10^{-6} M boundaries of the metastable minerals maghemite and freshly precipitated ferric hydroxide are shown as dashed lines on the diagram. It is quite certain that these two minerals are unstable with respect to hematite, pyrite, and magnetite and that, given sufficient time, will convert to the thermodynamically stable minerals. However, these minerals are clearly of more

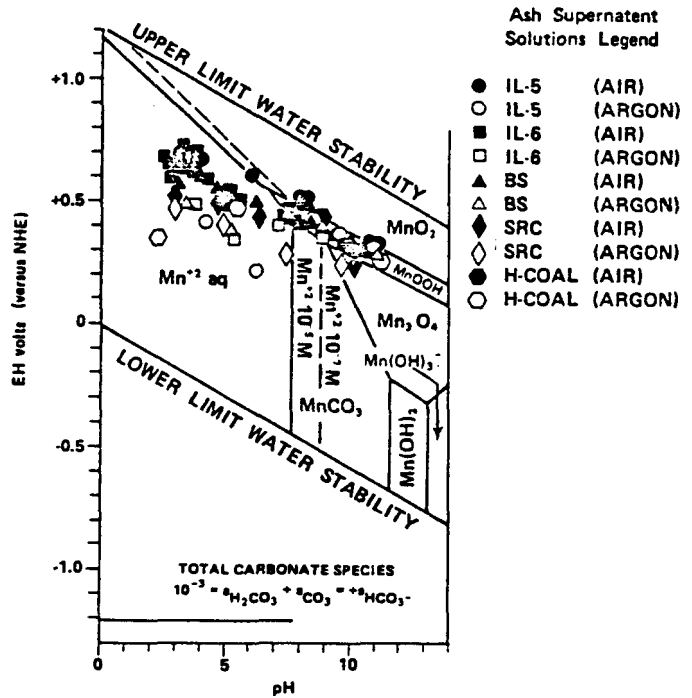


Figure 2. Stability relations of manganese oxides in water at 25°C.

than transitory existence in natural environments and warrant consideration as mineral phases likely to be the ones controlling iron concentrations during the initial leaching of solid wastes, which may likely be the environmentally critical period.

The data plotted in Figure 1 indicate that amorphous ferric hydroxide is a likely control on iron concentrations in the leachates at pH values less than 7. Indeed, computations of ion activity products for the leachates yield good agreement with the solubility constant for the amorphous ferric hydroxide in the acid solutions.

The iron concentrations tend to drop below detectable levels in the alkaline solutions.

It is clear from the plot of the data in Figure 1 that the Eh-pH relations of the alkaline leachates are not being controlled by equilibria between minerals shown on the diagram. Figure 2 shows the aqueous stability relations of the manganese oxide-carbonate system. The data indicate that the manganese oxides and carbonate are in equilibrium in the alkaline leachates while the data points for the acid leachates fall in the aqueous Mn^{+2} ion field. This conclusion is supported by the computations of the ion activity products for the manganese minerals. These computations showed that the alkaline solutions were generally in equilibrium with the manganese oxides or carbonate on which boundary the particular data points shown in the diagram fell. The acid leachates were undersaturated with respect to the various manganese minerals, as was deduced from Figure 2. Thus, it appears that manganese oxides are controlling the Eh-pH relations of the alkaline leachates and metastable freshly precipitated ferric hydroxide in the acid leachates.

The solubility relations of anhydrite and gypsum are shown in Figure 3. Here the solubility of gypsum is exerting a dominant influence over calcium and sulfate concentrations in the leachates at all pH levels, with the exception of the H-Coal leachates. The H-Coal leachates are all undersaturated with respect to gypsum but gypsum still provides the upper boundary for prediction of calcium and sulfate concentrations. This is of particular note since the H-Coal residue contained the highest concentrations of sulfur but had the lowest water soluble sulfur levels, including all sulfur species considered. This underscores the need for information on mineral forms in the solid waste in addition to chemical analysis of the waste.

The calcium and magnesium carbonate equilibria of alkaline (pH >7.6) leachates from the five solid wastes in contact with air are shown in Figure 4. Calcium concentrations of the acid leachates were controlled by gypsum equilibria, but it would be expected that calcium concentrations in alkaline solutions in contact with atmospheric carbon dioxide would be controlled by calcite solubility. However, the data plotted in Figure 4 indicate that the solutions are supersaturated with respect to calcite while some samples are either in equilibrium with or undersaturated with respect to magnesite. Other workers have also noted higher solubility of calcite in the presence of Mg. Hasset and Jurinak²¹ found that calcites with low levels of Mg showed an increase in solubility. Likewise, Berner²² showed that incorporation of Mg within the calcite to be considerably more soluble than pure calcite. Further, the presence of Mg and SO_4 have been shown by Akin and Lagerwerff²³ to enhance the solubility of calcite. Thus it appears that magnesite equilibria in alkaline leachates can be used to predict the upper bounds on Mg concentrations but that problems with supersaturation preclude the use of calcite to make similar predictions of Ca concentrations.

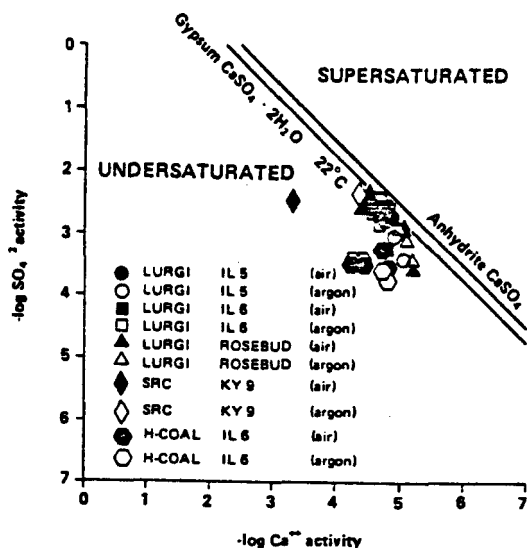


Figure 3. Calcium sulfate equilibria of leachates from five coal conversion solid wastes.

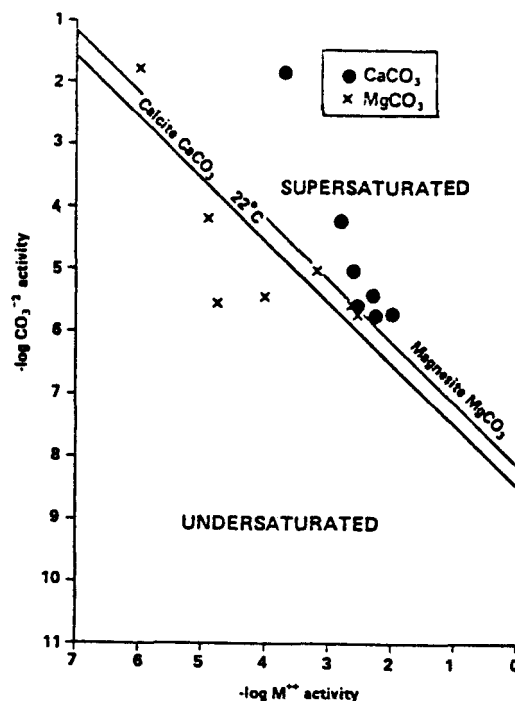


Figure 4. Calcium and magnesium carbonate equilibria of alkaline (pH >7.6) leachates from five coal conversion solid wastes in contact with air.

The silicon dioxide and aluminum hydroxide solubility equilibria are shown in Figure 5. Most samples were found to fall within the range of Si solubilities expected from amorphous glass and quartz. This is consistent with the experimental design, which employed glass carboys as the equilibration vessel and in which quartz was identified as being present in all the solid wastes. Amorphous SiO_2 is clearly not the most stable phase, and silica concentrations, after long time periods, would be expected to be controlled by aluminosilicate minerals or quartz.

The Al equilibria in the mid-acid and alkaline (not shown) pH range were dominated by the amorphous hydroxide. Similar to the Fe and Si equilibria, a metastable mineral phase was apparently controlling the solubility. It is clear that these metastable mineral phases must be considered when predicting the environmental impact during the initial leaching of coal conversion solid wastes.

The aqueous chemistry of some other potential contaminants was examined. For example, computation of ion activity products for BaSO_4 indicated that Ba concentrations in the leachates would never exceed 0.1 ppm, even in very acid solutions. Fluoride concentrations in the leachates were predicted to be controlled by precipitation of fluorite (CaF_2) and fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$). Phosphate levels in the alkaline leachates would never exceed 1 ppb; this was predicted from the ion activity product calculations for fluorapatite and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$). In the acid leachates, phosphate levels are predicted to be controlled by precipitation of insoluble iron and manganese phosphates.

The results of this study have other implications concerning heavy metals. The data strongly suggest that removal of trace metals such as Cd, Co, Cr, Cu, Ni, Pb, and Zn from slurry pond leachates may be controlled by adsorption on or coprecipitation with iron, manganese, and aluminum oxides and hydroxides. The removal of trace metals by this mechanism would be operative for long time periods because the adsorptive capacity of the solid phase would be continually replenished by formation of new metal oxides in the leachates. In any case, the partitioning between trace metals and solid phases must be considered when evaluating trace metal mobility in these systems. Further, these studies show that sulfate and carbonate are the major inorganic ligands that must be considered.

Thus, application of thermochemical solubility models to the coal solid waste leachates examined in this study has yielded some valuable insights into the potential pollution hazards of these wastes. It has shown that, while the concentrations of chemical constituents in the solid wastes and leachates varied over a wide range, similar mineral phases controlled the aqueous solubility of many major, minor, and trace ionic species for all five of the solid wastes.

ACKNOWLEDGMENTS

We gratefully acknowledge the U.S. Environmental Protection Agency, Fuel Process Branch, Research Triangle Park, North Carolina, for partial support of this work under Contract 68-02-2130, Characterization of Coal and Coal Residues. We also are indebted to the Peabody Coal Company, Freeburg, Illinois; to Hydrocarbon Research Inc., Trenton, New Jersey; and to Pittsburg and Midway Coal Mining Co., Fort Lewis, Washington, for supplying us with samples.

The authors are indebted to G. V. Smith, C. C. Hinkley, and M. Saporoschenko of Southern Illinois University, Carbondale, for Mössbauer Spectroscopic Analysis of the samples. The authors also wish to thank the Analytical Chemistry Section of the Illinois State Geological Survey under the direction of Dr. R. R. Ruch and to thank Dr. H. D. Glass and T. M. Johnson for assistance in portions of this research.

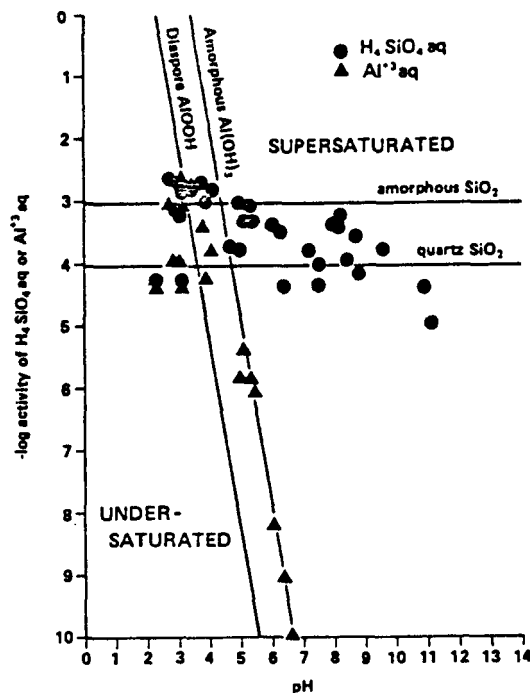


Figure 5. Silicon dioxide and aluminum hydroxide solubility equilibria of leachates from five coal conversion solid wastes.

REFERENCES

1. Cavanaugh, E. C., and W. C. Thomas. 1977. Environmental Assessment of Low/Medium BTU Gasification: Annual Report. US Environmental Protection Agency Publication No. EPA-600/7-77-142, Washington, D.C.
2. Cavanaugh, E. C., W. E. Corbett, G. C. Page. 1977. Environmental Assessment Data Base for Low/Medium BTU Gasification Technology. US Environmental Protection Agency Publication No. EPA-600/7-77-125a, Washington, D.C.
3. Somerville, M. H. and J. L. Elder. 1978. A comparison of trace metal analyses of North Dakota lignite laboratory ash with Lurgi gasifier ash and their use in environmental analysis. In F. A. Ayer (ed.), Environmental Aspects of Fuel Conversion Technology III, U.S. Environmental Protection Agency Publication No. EPA-600/7-78-063. Research Triangle Park, North Carolina.
4. Filby, R. H., K. R. Shah, and C. A. Sautter. 1978. Trace elements in the Solvent Refined Coal Process. In F. A. Ayer, (ed.), Environmental Aspects of Fuel Conversion Technology III, U.S. Environmental Protection Agency Publication No. EPA-600/7-78-063. Research Triangle Park, North Carolina.
5. Sinor, J. E. 1977. Evaluation of background data relating to new source performance standards for Lurgi gasification. US Environmental Protection Agency Publication No. EPA-600/7-77-057, Washington, D.C.
6. Griffin, R. A., R. M. Schuller, J. J. Suloway, S. J. Russell, W. F. Childers, and N. F. Shimp. 1978. Solubility and toxicity of potential pollutants in solid coal wastes. In F. A. Ayer, (ed.), Environmental Aspects of Fuel Conversion Technology III, US Environmental Protection Agency Publication No. EPA-600/7-78-063. Research Triangle Park, North Carolina.
7. Ruch, R. R., H. J. Gluskoter, and J. E. Kennedy. 1971. Mercury content of Illinois coals. Illinois State Geological Survey Environmental Geology Note 43, 15 pp.
8. Ruch, R. R., H. J. Gluskoter, and N. F. Shimp. 1973. Occurrence and Distribution of Potentially Volatile Trace Elements in Coal: An Interim Report. Illinois State Geological Survey Environmental Geology Note 61, 43 p.
9. Ruch, R. R., H. J. Gluskoter, and N. F. Shimp. 1974. Occurrence and Distribution of Potentially Volatile Trace Elements in Coal: A Final Report. Illinois State Geological Survey Environmental Geology Note 72, 96 p.
10. Gluskoter, H. J. 1975. Mineral Matter and Trace Elements in Coal, In Babu (ed.), "Trace Elements in Fuel," Advances in Chemistry Series 141, American Chem. Soc., p. 1-22.
11. Gluskoter, H. J., R. R. Ruch, W. G. Miller, R. A. Cahill, G. B. Dreher, and J. K. Kuhn. 1977. Trace Elements in Coal: Occurrence and Distribution. Illinois State Geological Survey Circular 499.
12. Braunstein, H. M., E. D. Copenhaver, and H. A. Pfudere. 1977. "Environmental, Health, and Control Aspects of Coal Conversion: An Information Overview," Oak Ridge National Laboratory, ORNL/EIS-94 and 95, vols. 1 and 2.

13. Parker, Leon C. and Dewey L. Dykstra. 1978. "Environmental Assessment Data Base for Coal Liquefaction Technology." EPA-600/7-78-184a and 184b, September, 1978.
14. Schuller, R. M., J. J. Suloway, R. A. Griffin, S. J. Russell, and W. F. Childers. 1979. Identification of potential pollutants from coal conversion wastes. Proceedings of the Society of Mining Engineers--American Institute of Mining Engineers Annual Meeting, February 18-22, 1979, New Orleans.
15. Griffin, R. A., R. M. Schuller, J. J. Suloway, N. F. Shimp, and W. F. Childers. 1979. Potential pollution hazards from coal solid wastes. Final report for US Environmental Protection Agency Contract 68-02-2130, Task D, Research Triangle Park, North Carolina.
16. Environmental Protection Agency. 1972. 1972 Water Quality Criteria. US Environmental Protection Agency R3-73-033, Washington, D.C.
17. Garrells, R. M., and C. L. Christ. 1965. "Solutions, Minerals, and Equilibria," Harper and Row, New York, N.Y.
18. Truesdell, A. H., and B. F. Jones. 1973. WATEQ, a computer program for calculating chemical equilibria on natural waters. National Technical Information Service P.B. 220464.
19. Truesdell, A. H., and B. F. Jones. 1974. WATEQ, a computer program for calculating chemical equilibria on natural waters. U.S. Geol. Survey Jour. Research. 2:233-248.
20. Plummer, N. L., B. F. Jones, and A. H. Truesdell. 1976. WATEQF--A Fortran IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. U.S. Geological Survey Water-Resources Investigations 76-13, NTIS No. PB-261-027.
21. Hassett, J. J. and J. J. Jurinak. 1971. Effect of Mg^{+2} ion on the solubility of solid carbonates. Soil Sci. Soc. Am. Proc. 35:403-406.
22. Berner, R. A. 1975. The role of magnesium in the crystal growth of calcite and aragonite from sea water. Geochimica et Cosmochimica Acta 39:489-504.
23. Akin, G. W., and J. V. Lagerwerff. 1965. Calcium carbonate equilibria in solutions open to the air. II. Enhanced solubility of $CaCO_3$ in the presence of Mg^{+2} and SO_4^{-2} . Geochimica et Cosmochimica Acta 29:253-260.

A P P E N D I X D
MOSSBAUER SPECTROSCOPIC STUDIES OF THE
MINERALOGICAL CHANGES IN COAL AS A FUNCTION
OF CLEANING, PYROLYSIS, COMBUSTION AND
COAL CONVERSION PROCESSES

MÖSSBAUER SPECTROSCOPIC STUDIES OF THE MINERALOGICAL
CHANGES IN COAL AS A FUNCTION OF CLEANING, PYROLYSIS,
COMBUSTION AND COAL CONVERSION PROCESSES

M. Saporoschenko
Department of Physics and Astronomy
Southern Illinois University
Carbondale, Illinois 62901

C. C. Hinckley, G. V. Smith, and H. Twardowska
Department of Chemistry and Biochemistry
Southern Illinois University
Carbondale, Illinois 62901

and

R. H. Shiley, R. A. Griffin, and S. J. Russell
Illinois State Geological Survey
Urbana, Illinois 61801

August 22, 1979

ABSTRACT

The mineralogical changes in a Perry County, Illinois coal from the Herrin (No. 6) Member as a function of cleaning, pyrolysis, combustion, and coal conversion processes have been studied. This study employed Mössbauer spectroscopy in tandem with X-ray diffraction to follow the fate of the iron present in the coal during processing.

The chemistry of the pyrite conversion as revealed by this study is less complex than was expected. Iron does not become uniformly distributed among all possible sites, but exhibits preferences which are in effect simplifying. The detailed distribution of iron is dependent upon the particular process equipment in which the coal is used or on the conversion process in which it is being used.

INTRODUCTION

Recently, Hinckley et al.^{1/} completed a Mössbauer study of the iron in Lurgi gasification ashes and power plant fly and bottom ashes. That study indicated that Fe⁵⁷ Mössbauer spectroscopy was an excellent tool for the study of iron in coal ashes, water-quenched molten bottom ash, and coal-related waste products. When Mössbauer spectroscopic methods were combined with X-ray diffraction techniques, very detailed descriptions of the mineral phases of iron and iron distribution could be made.

As a result of the success in applying the combination of Mössbauer and X-ray diffraction techniques in the study by Hinckley et al.^{1/}, an attempt to characterize the iron species and the mineralogical changes within a related group of coal solid wastes was undertaken. The following

Perry County, Illinois coal from the Herrin (No. 6) Member and derived waste products were used for this study.

1. A sample washed at the mine.
2. The slurry (fines) from the washing plant.
3. The coarse refuse (gob) from the preparation plant (from high sulfur No. 6 Coal).
4. A medium temperature char (650°C) from a sole heated expansion-contraction oven.
5. A high temperature (990°C) char made in the Illinois State Geological Survey coke oven.
6. A fly ash from a pulverized fuel power plant.
7. An ash from the Westfield, Scotland, Lurgi gasification plant.
8. A mineral residue from the vacuum still in the H-coal[®] liquefaction process.

Other samples studied included are:

1. A prepared coal from the Springfield (No. 5) Member from Perry County, Illinois.
2. Coarse refuse (gob) from a coal preparation plant in Jefferson County, Illinois (a low sulfur No. 6 Coal).
3. The mineral residue from an SRC liquefaction process when processing a Hopkins County, Kentucky, No. 9 Coal.

EXPERIMENTAL

Mössbauer Spectroscopy

Mössbauer spectra were obtained with an Austin Science Associates spectrometer utilizing a linear acceleration motor to move the source (⁵⁷Co

in Pd). The spectra were collected with a Nicolet 1070 N Signal Averager with 1024 channels. Two spectra were collected simultaneously and were combined to yield a spectrum which was recorded in 512 channels. The spectra were obtained at room temperature and recorded until approximately 5×10^6 counts per channel in the baseline had been accumulated.

Mössbauer spectra were analyzed by the use of a least squares fit of lorentzian-shaped multiplets to the observed spectrum using the computer program MOSFIT. Each iron absorption is described in terms of one to six lorentzian curves with the parameters: isotope shift, S ; quadrupole coupling constant, E ; and internal magnetic field (when present), M . Within each species multiplet, line width and intensity parameters were set equal for each absorption. Magnetically split absorptions had intensity ratios of 3:2:1:1:2:3. These restraints were employed because of the large number of components typically found in the spectra. Percentage figures were based upon the calculated areas of the absorption curves and should be viewed as approximate values. We have applied these techniques in previous studies of coal,^{3/} ash,^{1/} and oil shale^{4/}.

X-ray Diffraction Analysis

The mineral composition of the samples was determined by X-ray diffraction using a Phillips Norelco Diffraction Unit. The powdered samples were scanned at $2^\circ 2\theta/\text{minute}$ with copper $K\alpha$ radiation.

RESULTS AND DISCUSSION

This study employs Mössbauer spectroscopy to follow the fate of the iron, which is present in the coal, during processing. The Illinois No. 6 is a useful coal for the study because after washing, virtually all of the

retained iron is in pyrite. Thus, the determination of iron components in the various processing residues indicates what happens to pyritic iron in the process with a minimum of interferences. Silicate minerals are also present but are not iron bearing and, therefore, are not observed by Fe^{57} Mössbauer spectroscopy. Other iron-bearing minerals expected to be present in the coal are very effectively removed in the washing process. These species were identified by the Mössbauer studies of the washing refuse.

Combined results of mineralogical and iron Mössbauer analyses are presented in table 1. Mössbauer assignments are based upon parameter values (table 2) reported in reference publications^{5/} or determined from standards.

The Mössbauer spectra for the Perry County Illinois No. 6 Coal is shown in figure 1. Typically, the major iron-containing component in this coal is pyrite and a small amount of iron (Fe^{+2}) is present in illite. Since this was a washed sample, some of the soluble iron-bearing minerals such as sulfates, if present in the coal before washing, may have been removed. Sulfates in coal are primarily oxidation products of pyrite which form when coal is exposed to moisture and the atmosphere. A coal slurry from the washing plant contains pyrite and illite. Nearly 6 percent of the iron found in the slurry was associated with illite while only 0.2 percent of the iron was associated with illite in the washed coal. Although hydrated ferrous sulfate was found in the slurry by X-ray diffraction analysis, it was not found by Mössbauer spectroscopy. This could be due to oxidation during the time between the two analyses.

In comparison, the Perry County Illinois No. 5 Coal also has pyrite as its major iron species, but in this case ferrous sulfate rather than illite iron species were found. X-ray diffraction analysis does, however, show the presence of some illite in the coal.

Mössbauer spectra of a preparation plant coarse refuse from low-sulfur Jefferson County Illinois No. 6 Coal (figure 2) indicated that two ferric and two ferrous iron species were present. The two ferric and one ferrous species were assigned to illite. The remaining ferrous species was an iron carbonate. X-ray diffraction data indicated the presence of a trace of pyrite and melanterite in this sample, although it was not found in the Mössbauer analysis.

The principal iron compound in the gob from high-sulfur Perry County Illinois No. 6 Coal (figure 3) was pyrite. The component with the next higher percentage was a ferric species which, together with one of the ferrous species, was assigned to illite. Ferrous sulfate was present in smaller quantities than the other species.

Comparison of the high- and low-sulfur coal preparation plant samples was instructive. X-ray diffraction analyses indicated that the two samples have several minerals in common that may serve as host lattices for iron such as plagioclase feldspar and calcite. The Mössbauer spectra indicated iron species with quite distinct parameters which do not include the plagioclase feldspar, but showed the presence of an iron carbonate in the gob from the low-sulfur coal preparation plant but not from the high-sulfur preparation plant. Both refuses contained illite iron species. The high-sulfur refuse contained hydrated FeSO_4 and the low-sulfur refuse contained ferrous sulfate in the form of melanterite. These assignments were based upon a supporting study of natural iron-containing illites^{6/}. Though each of the illite species has parameters which fall within the ranges expected for iron in illite, the parameter values for the two samples were

different. Furthermore, there were two ferric illite species in the low-sulfur sample and only one in the high sulfur sample.

The Mössbauer spectrum of the Lurgi ash from the Perry County Illinois No. 6 Coal is shown in figure 4. Analysis of the ash indicates that approximately 60 percent of the ash was a mixture of the iron oxides-hematite, magnetite and goethite. The remainder of the iron species was associated with silicates and mullite.

Assignment of a Mössbauer absorption to an iron silicate species is a nonspecific identification because isotope shifts and quadrupole coupling constants vary widely for these species^{7/}. Iron silicate isotope shifts vary from 0.0 (measured versus iron foil) to 0.5 mm/sec for Fe^{+3} , and from 1.0 to 1.4 mm/sec for Fe^{+2} . Quadrupole coupling constants for iron silicates vary from 0.0 to 1.0 mm/sec for Fe^{+3} , and from 1.5 to 3.0 mm/sec for Fe^{+2} . The assignment means that silicate species are known to be present from X-ray and/or elemental analysis, that the assigned absorption is described by isotope shift and quadrupole coupling parameters which fall within the above ranges, and that these parameter values do not correspond to those of other known species.

The Lurgi ash sample included in this study is similar in nature to the ash derived from other oxidative processes (e.g. combustion) such as that obtained from a conventional power plant^{1/} using a Perry County No. 6 Coal (table 3). Each ash will be expected to have a composition that is dependent upon the nature of the coal utilized, but will also be affected by the conditions of the process. For instance, each boiler will produce an ash from a particular coal that is a function of the design and operating conditions of that particular boiler.

Mössbauer spectra of the medium (650°C) and high (990°C) temperature chars (coke) are shown in figures 5 and 6, respectively. Pyrite was found as the principal iron compound in both chars. It was found at concentrations of 46.8 percent and 49.3 percent, respectively. A considerable concentration of pyrrhotite (42.8 percent and 43.2 percent) along with smaller quantities of mullite (7.4 percent and 4.5 percent) was found. X-ray diffraction analysis and Mössbauer spectroscopy show the presence of hydrated ferrous sulfate in both chars.

In the charring process, the coal is heated at normal pressure in an enclosed vessel (reducing conditions) and without additives. This treatment can be contrasted with liquefaction processes in which the heating is accompanied by the addition of hydrogen at elevated pressures. The H-coal[®] (figure 7) and SRC residues were derived from such processes. In these latter samples, essentially all of the pyrite was converted to pyrrhotite.

Pyrrhotite was the principal iron-bearing component found in the H-coal[®] residue (figure 7). A small amount of iron was found in hydrated ferrous sulfate but no pyrite was found by either X-ray diffraction or Mössbauer spectroscopic analysis.

Mössbauer pyrrhotite assignments for the chars and the H-coal[®] residue were based upon X-ray diffraction findings of pyrrhotite in the samples, and upon the Mössbauer parameter values determined in fits of the spectra. These parameter values fall within ranges found for pyrrhotite in chars by Huffman and Huggins^{5/}.

Pyrrhotite spectra in the char and H-coal[®] samples are unusual; i.e., magnetic parameters determined from these spectra do not include the value 228K_{Oe} found in both monoclinic and hexagonal pyrrhotite and, further, a

magnetic parameter value around 310 KOe was found in all of them. This last is characteristic of troilite and suggests that pyrrhotite in these materials is a mixture of troilite and pyrrhotite. X-ray analysis, however, indicates only pyrrhotite. The nature of the mixture therefore remains unresolved.

The SRC residue contained iron principally in pyrrhotite. This sample also contained iron in hydrated ferrous sulfate and pyrite. Mössbauer parameter values for pyrrhotite in this sample were different from those of the H-coal[®] and the chars in that they fall within ranges characteristic of the natural pyrrhotite from Sudbury in Ontario, Canada, often used as a reference standard.

CONCLUSIONS

Pyrite was the major iron-containing component in the Perry County, Illinois No. 6 Coal. While only 0.2 percent of the iron in this washed coal was associated with illite, nearly 6 percent of the iron found in the slurry was associated with the illite. There appear to be no minerals present in this slurry that would adversely affect its use in combustion processes after additional cleaning in the preparation plant.

The gcb from the preparation plant contains pyrite and hydrated ferrous sulfate as well as a ferric and a ferrous iron species in the illite.

The chemistry of pyrite conversion revealed in this study was much less complex than might have been expected. Complete mineralogical analysis revealed many more substances present than was found using Mössbauer spectroscopy alone. Iron did not become uniformly distributed among all possible sites, but exhibited preferences which were essentially simplifying.

Still, the detailed distribution of iron for each conversion process was dependent upon the process to which the coal was subjected.

Table 3 summarizes the iron-bearing minerals in the coals and coal process residues. The changes in iron species are illustrated by the changes in the mineral composition of the samples.

Much of the iron in Lurgi ash was found in an oxide mixture which contained about 60 percent of the iron^{1/}. The remaining iron was present in mullite (Fe^{+3}) and other silicates (Fe^{+2}). The components of the Lurgi ash were broadly similar to those of the power plant fly ash.

Chars contained pyrite and pyrrhotite. Only the high temperature char contained a small amount of iron in mullite, but in a quantity consistent with the clay present in the original coal.

Liquefaction residues contained iron as pyrrhotite with small amounts of hydrated ferrous sulfate. The H-coal[®] residues contained no detectable pyrite while the SRC residue contained 10 percent. The chemistry of the liquefaction processes was apparently more effective in converting pyrite to pyrrhotite than was the chemistry of the charring process.

Comparison of the H-coal[®] and SRC residues and the chars is revealing in an additional way. Mössbauer parameters of pyrrhotite in the H-coal[®] residue were similar to those of the chars. Those parameters for the SRC residue were more characteristic of the natural pyrrhotite from Sudbury in Ontario Canada. This finding suggests that there are differences in the two cases which may depend upon the non-mineral matter in the samples. The carbonaceous matter in the residues provides the matrices for the iron compounds. Differences in Mössbauer parameters may indicate differences in interaction with those matrices and thus may be an important tool in future characterizations of coals used for liquefaction by various processes.

ACKNOWLEDGMENTS

This research was supported in part by the Southern Illinois University Coal Extraction and Utilization Research Center; by the Illinois State Geological Survey; and by the U.S. Environmental Protection Agency, Fuel Process Branch, Research Triangle Park, North Carolina under Contract 68-02-2130 to the University of Illinois, "Characterization of Coal and Coal Residues." We are indebted to D. R. Dickerson and R. J. Helfinstine of the Illinois State Geological Survey Staff for their valuable help in this research program. We are also indebted to the Peabody Coal Company, Freeburg, Illinois; to Hydrocarbon Research Inc., Trenton, New Jersey; and to Pittsburgh and Midway Coal Mining Co., Fort Lewis, Washington, for supplying us with samples.

REFERENCES

1. C. C. Hinckley, G. V. Smith, H. Twardowska, M. Saporoschenko, R. H. Shiley, and R. A. Griffin, "Mössbauer Studies of Iron in Lurgi Gasification Ashes and Power Plant Fly and Bottom Ash," Submitted to Fuel (1979).
2. G. M. Bancroft, "Mössbauer Spectroscopy--An Introduction for Inorganic Chemists and Geochemists," John Wiley and Sons, New York, (1973).
3. G. V. Smith, J. H. Liu, M. Saporoschenko and R. H. Shiley, Fuel, 57, 41 (1978).
4. R. D. Cole, J. H. Liu, G. V. Smith, C. C. Hinckley and M. Saporoschenko, Fuel, 57, 514 (1978).
5. G. P. Huffman and F. E. Huggins, Fuel, 57, 592 (1978) and references quoted therein.
6. C. C. Hinckley, unpublished results.
7. G. M. Bancroft, A. G. Maddock, and R. G. Burnes, Geochim. Cosmochim. Acta, 31, 2219 (1967).

FIGURE CAPTIONS

- Figure 1. The ^{57}Fe Mössbauer spectrum of a Perry County Illinois No. 6 Coal. 5-mm thick chunk.
- Figure 2. The ^{57}Fe Mössbauer spectrum of the coarse refuse (gob) from a coal preparation plant in Jefferson County, Illinois, using a low-sulfur coal.
- Figure 3. The ^{57}Fe Mössbauer spectrum of the coarse refuse (gob) from a coal preparation plant using a high-sulfur Perry County Illinois No. 6 Coal.
- Figure 4. The ^{57}Fe Mössbauer spectrum of an ash from the Westfield, Scotland, Lurgi gasification plant using a Perry County Illinois No. 6 Coal.
- Figure 5. The ^{57}Fe Mössbauer spectrum of a medium temperature char (650°C) from a sole-heated expansion-contraction oven using a Perry County Illinois No. 6 Coal.
- Figure 6. The ^{57}Fe Mössbauer spectrum of a high temperature char (990°C) made in the Illinois State Geological Survey coke oven using a Perry County Illinois No. 6 Coal.
- Figure 7. The ^{57}Fe Mössbauer spectrum of a mineral residue from the vacuum still in the H-coal[®] liquefaction process using a Perry County Illinois No. 6 Coal.

Table 1. Minerals identified in coal, coal solid wastes, and coal conversion process mineral residues

No. 5 Coal (Perry County, IL)

Pyrite	FeS ₂	Mössbauer, X-ray
Ferrous sulfate	FeSO ₄	Mössbauer
Quartz	SiO ₂	X-ray
Illite	K,Al-silicate-clay	X-ray
Kaolinite	Al-silicate-clay	X-ray
Expandable clays	Na,K,Ca,Al-silicates	X-ray
Calcite	CaCO ₃	X-ray

No. 6 Coal (Perry County, IL)

Pyrite	FeS ₂	Mössbauer, X-ray
Quartz	SiO ₂	X-ray
Illite	Fe ⁺² ,K,Al-silicate-clay	Mössbauer, X-ray
Kaolinite	Al-silicate-clay	X-ray
Expandable clays	Na,K,Ca,Al-silicates	X-ray
Calcite	CaCO ₃	X-ray

Coarse refuse (gob) from high-sulfur No. 6 Coal (Perry County, IL)

Pyrite	FeS ₂	Mössbauer, X-ray _{1/}
Illite	Fe ⁺² ,Fe ⁺³ ,K,Al-silicate-clay	Mössbauer, X-ray _{1/}
Hydrated ferrous sulfate	FeSO ₄	Mössbauer, X-ray
Plagioclase feldspar	Na,Ca,Al-silicate	X-ray
Calcite	CaCO ₃	X-ray
Kaolinite	Al-silicate-clay	X-ray
Quartz	SiO ₂	X-ray

Coarse refuse (gob) from low-sulfur No. 6 Coal (Jefferson County, IL)

Pyrite (trace)	FeS ₂	X-ray
Illite (three species)	Fe ⁺³ ,Fe ⁺³ ,Fe ⁺² ,K,Al-silicate-clay	Mössbauer, X-ray _{1/}
Quartz	SiO ₂	X-ray
Plagioclase feldspar	Na,Ca,Al-silicate	X-ray
Calcite	CaCO ₃	X-ray
Sphalerite	ZnS	X-ray
Kaolinite	Al-silicate-clay	X-ray
Melanterite	FeSO ₄ ·7H ₂ O	X-ray
Iron carbonate	FeCO ₃	Mössbauer

Medium-temperature char (650°C) from No. 6 Coal (Perry County, IL)

Pyrrhotite	Fe _{1-x} S	Mössbauer, X-ray
Pyrite	FeS ₂	Mössbauer, X-ray
Hydrated ferrous sulfate	FeSO ₄	Mössbauer, X-ray
Calcite	CaCO ₃	X-ray
Illite	Fe ⁺² ,K,Al-silicate-clay	Mössbauer, X-ray
Plagioclase feldspar	Na,Ca,Al-silicate	X-ray
Quartz	SiO ₂	X-ray
Anhydrite	CaSO ₄	X-ray

Table 1. (Cont.)

High-temperature char (990°C) No. 6 Coal (Perry County, IL)

Pyrrhotite	$Fe_{1-x}S$	Mössbauer, X-ray
Pyrite	FeS_2	Mössbauer, X-ray
Mullite	$Fe^{+2}, 3Al_2O_3 \cdot 2SiO_2$	Mössbauer
Quartz	SiO_2	X-ray
Hydrated ferrous sulfate	$FeSO_4$	Mössbauer, X-ray

LURGI Ash^{2/} from No. 6 Coal (Illinois)

Hematite	Fe_2O_3	Mössbauer, X-ray
Goethite	$\alpha-FeO \cdot OH$	Mössbauer
Quartz	SiO_2	X-ray
Plagioclase feldspar	Na, Ca, Al-silicate	X-ray
Mullite	$Fe^{+3}, 3Al_2O_3 \cdot 2SiO_2$	Mössbauer, X-ray
Magnetite	Fe_3O_4	Mössbauer
Silicate (glass)	Fe^{+2}	Mössbauer

H-Coal[®] residue from No. 6 Coal (Perry County, IL)

Pyrrhotite	$Fe_{1-x}S$	Mössbauer, X-ray
Calcite	$CaCO_3$	X-ray
Quartz	SiO_2	X-ray
Kaolinite	Al-silicate-clay	X-ray
Expandable clays	Na, K, Ca, Al-silicate	X-ray
Hydrated ferrous sulfate	$FeSO_4$	Mössbauer, X-ray

SRC liquefaction process dry mineral residue
No. 9 Coal (Hopkins County, KY)

Pyrrhotite	$Fe_{1-x}S$	Mössbauer, X-ray
Kaolinite	Al-silicate-clay	X-ray
Expandable clay	Na, K, Ca, Al-silicate	X-ray
Pyrite	FeS_2	Mössbauer
Quartz	SiO_2	X-ray
Hydrated ferrous sulfate	$FeSO_4$	Mössbauer, X-ray

Coal slurry (fines) from the washing plant (Perry County, IL)

Pyrite	FeS_2	Mössbauer, X-ray
Illite	Fe^{+2}, K, Al -silicate-clay	Mössbauer, X-ray
Kaolinite	Al-silicate-clay	X-ray
Hydrated iron-sulfates	$FeSO_4$	X-ray
Quartz	SiO_2	X-ray
Anhydrite	$CaSO_4$	X-ray
Feldspar	Na, Ca, Al-silicate	X-ray
Calcite	$CaCO_3$	X-ray
Bassanite	Hydrated calcium sulfate	X-ray

1/ Can not distinguish between the valence states of iron

2/ C. C. Hinckley, 1979. Reference No. 1

Table 2. Mössbauer parameters for iron species in coals and coal process residues^{a,b,c}

Assignment	S (mm/sec)	E (mm/sec)	M (KOE)	% Fe
<u>No. 5 Coal (Perry County, IL)</u>				
Pyrite	0.304(1)	0.618(1)		95.9
Ferrous sulfate	1.18 (2)	2.92 (3)		4.1
<u>No. 6 Coal (Perry County, IL)</u>				
Pyrite	0.305(8)	0.622(1)		99.8
Illite Fe ⁺²	1.26 (3)	2.79 (2)		0.2
<u>Coal slurry (fines) from washing plant No. 6 Coal (Perry County, IL)</u>				
Pyrite	0.311(1)	0.652(1)		94.2
Illite Fe ⁺²	1.24 (2)	2.66 (4)		5.8
<u>Coarse refuse (gob) from a low-sulfur No. 6 Coal (Jefferson County, IL)</u>				
Illite Fe ⁺³	0.20 (1)	0.88 (2)		29.0
Illite Fe ⁺³	0.17 (3)	0.32 (9)		24.6
Illite Fe ⁺²	1.256(4)	2.56 (2)		29.3
Iron carbonate	1.38 (2)	1.59 (4)		17.0
<u>Coarse refuse (gob) from a high-sulfur No. 6 Coal (Perry County, IL)</u>				
Pyrite	0.306(1)	0.616(1)		88.0
Illite Fe ⁺³	0.407(4)	1.142(4)		6.9
Illite Fe ⁺²	1.06 (2)	2.64 (4)		2.4
Ferrous sulfate	1.171(7)	2.956(8)		2.6
<u>Medium-temperature char (650°C) No. 6 Coal (Perry County, IL)</u>				
Pyrrhotite	0.788(8)	-0.230(4)	315(2)	7.8
Pyrrhotite	0.74 (1)	-0.04 (1)	305(3)	16.0
Pyrrhotite	0.735(8)	0.100(9)	274(4)	9.0
Pyrrhotite	0.73 (1)	0.24 (1)	251(4)	10.0
Pyrite	0.36 (1)	0.634(2)		48.0
Illite Fe ⁺²	0.999(9)	2.39 (2)		7.4
Ferrous sulfate	1.24 (1)	2.56 (2)		3.0
<u>High-temperature char (990°C) No.6 Coal (Perry County, IL)</u>				
Pyrrhotite	0.769(9)	-0.172(9)	313(2)	9.7
Pyrrhotite	0.758(9)	-0.05 (1)	304(3)	12.3
Pyrrhotite	0.727(7)	0.066(9)	277(4)	10.0
Pyrrhotite	0.76 (1)	0.13 (1)	247(5)	11.2
Pyrite	0.34 (1)	0.634(5)		49.3
Mullite Fe ⁺²	1.013(9)	2.26 (3)		4.5
Ferrous sulfate	1.32 (1)	2.44 (5)		3.0
<u>H-Coal³ No. 6 Coal (Perry County, IL)</u>				
Pyrrhotite	0.78 (1)	-0.146(6)	311(6)	51.8
Pyrrhotite	0.82 (1)	0.048(9)	301(5)	7.3
Pyrrhotite	0.79 (1)	0.048(9)	287(5)	7.6
Pyrrhotite	0.75 (1)	0.144(8)	268(4)	30.2
Ferrous sulfate	1.24 (2)	2.59 (3)		2.6

Table 2. (Cont.)

Assignment	S (mm/sec)	E (mm/sec)	M (KOe)	% Fe
<u>SRC from a No. 9 Coal^{d/} (Hopkins County, KY)</u>				
Pyrrhotite	0.713(7)	0.11 (1)	302(6)	16.8
Pyrrhotite	0.750(9)	0.09 (2)	290(5)	11.8
Pyrrhotite	0.743(5)	0.09 (1)	268(4)	35.6
Pyrrhotite	0.693(9)	0.14 (2)	239(7)	16.4
Pyrite	0.370(6)	0.70 (1)		9.4
Ferrous sulfate	1.25 (1)	2.62 (2)		9.9

^aTabulations by column headings; S, isotope shift;
E, quadrupole coupling constant; M, internal magnetic field; %, percent iron

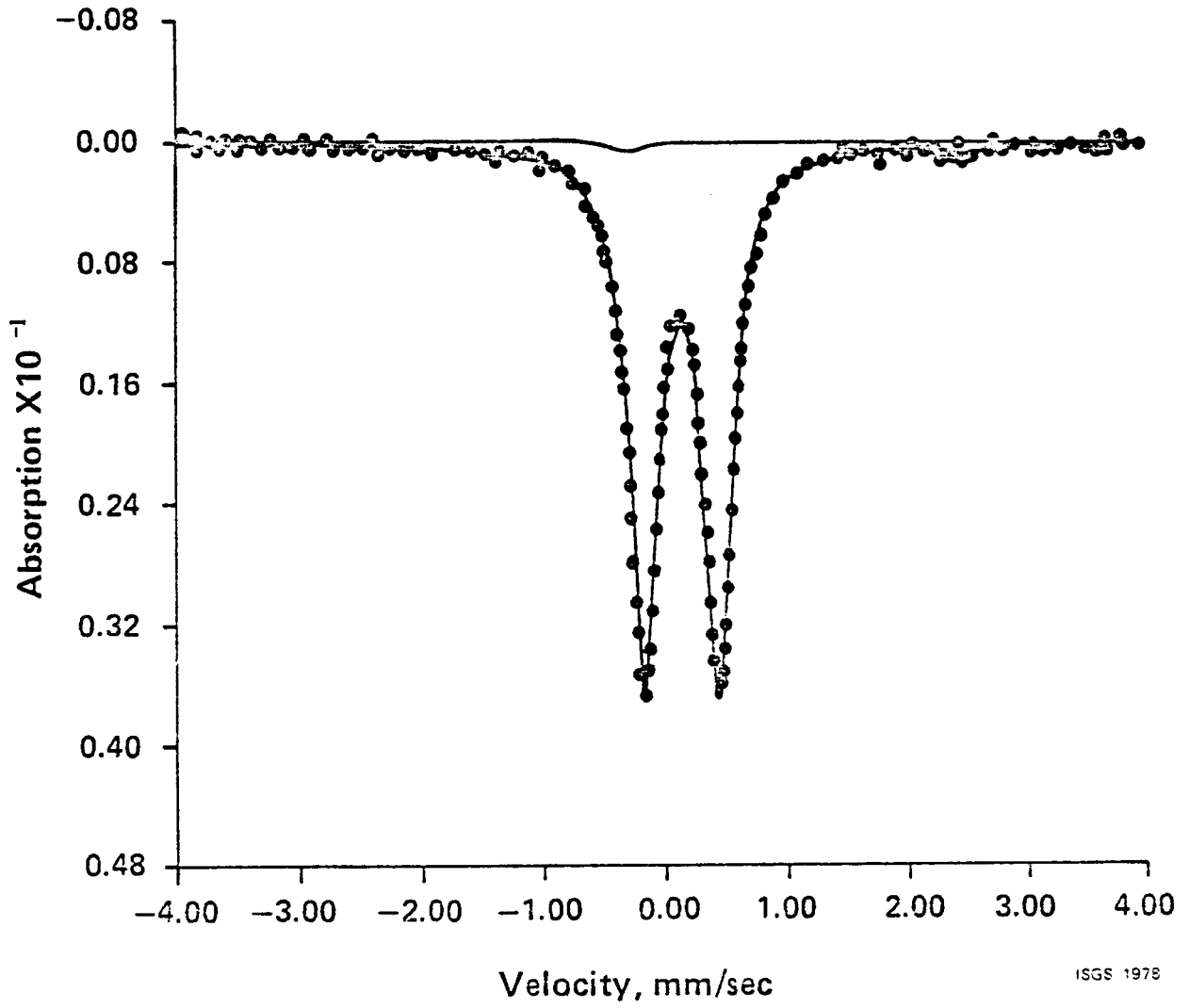
^bError factors in last digit given in parenthesis, as; 5.73(5) is 5.73±0.05

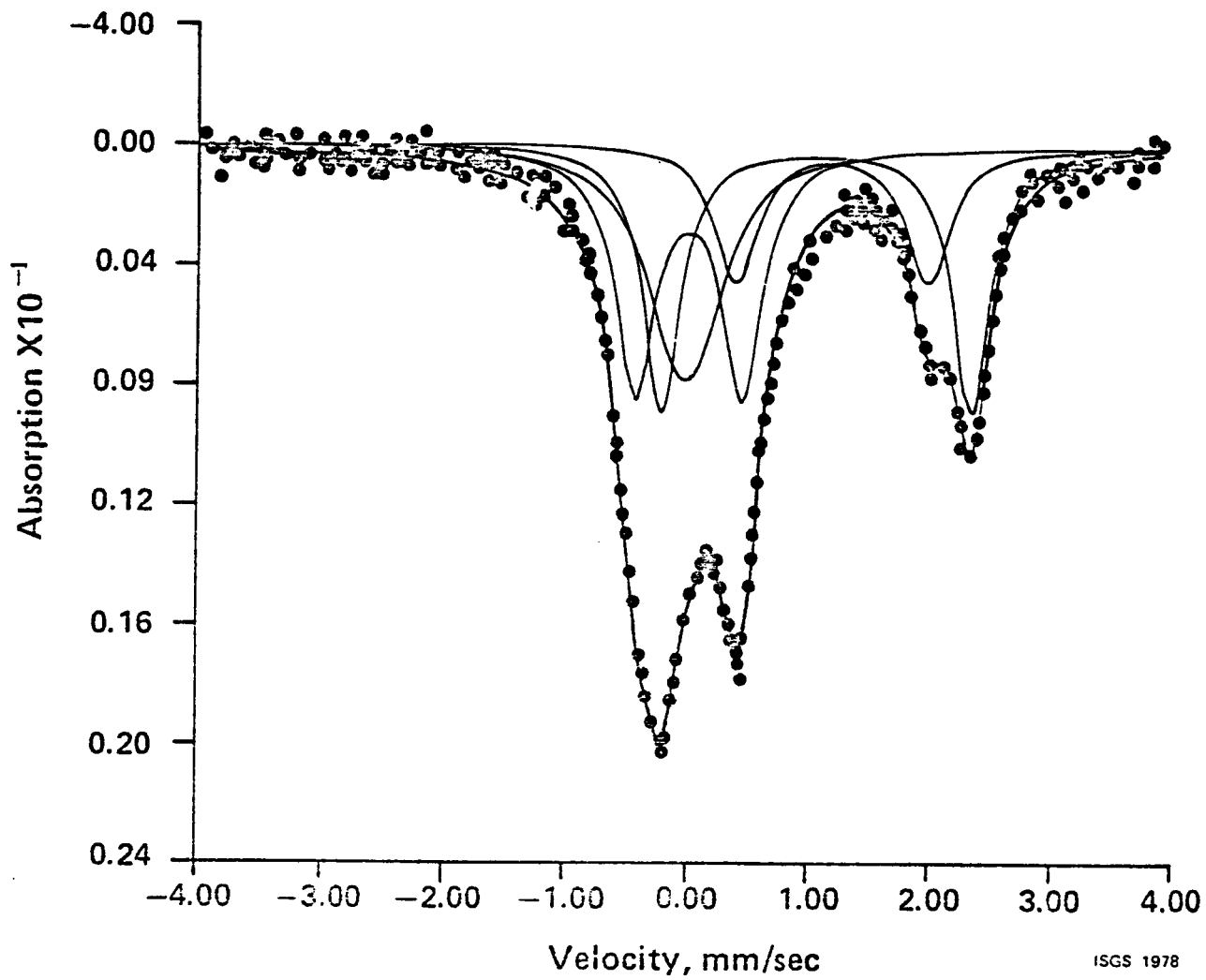
^cShifts reported versus NBS iron foil

^dCorelated with Herrin (No. 6) Coal of Illinois

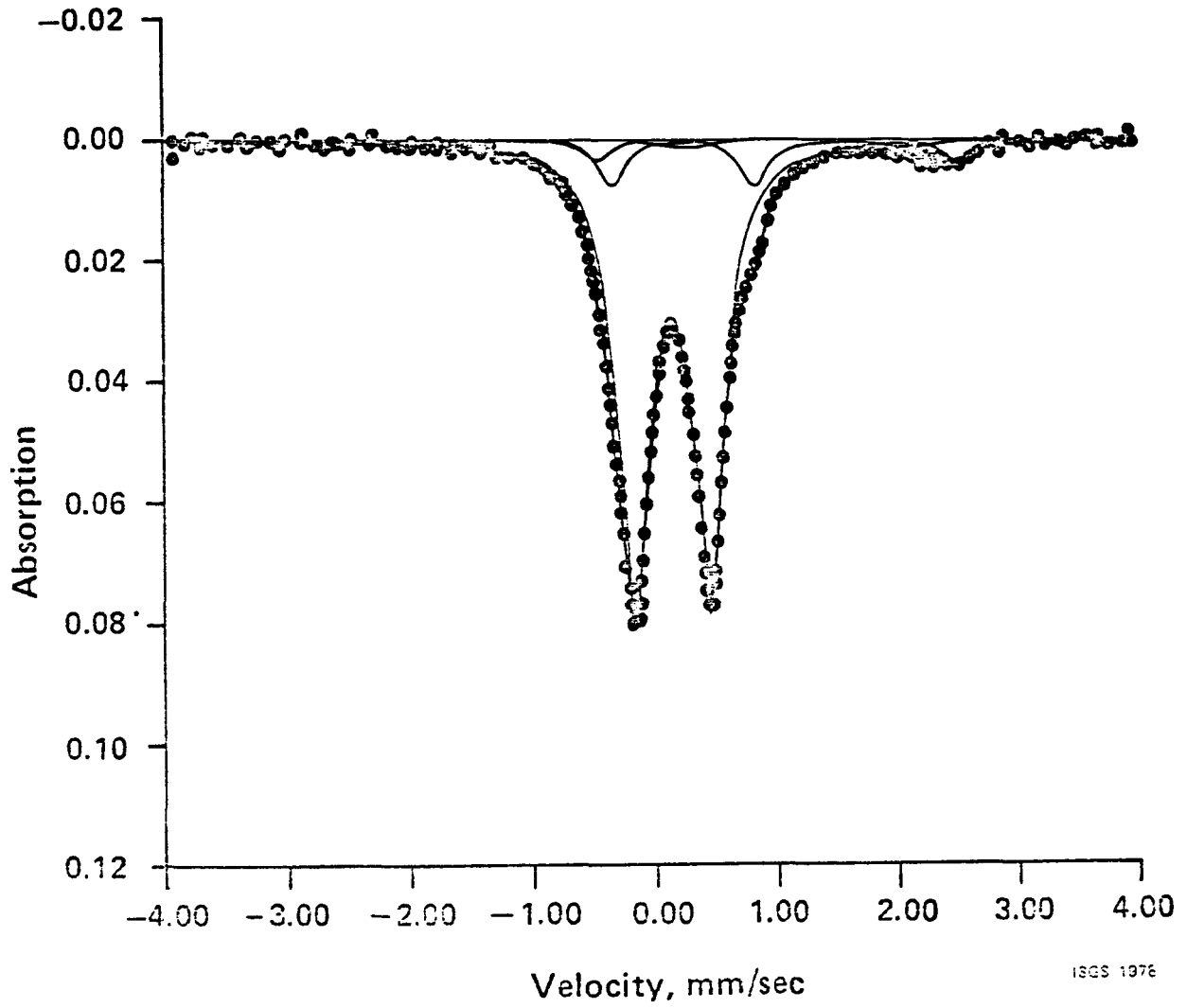
Table 3. Iron-bearing minerals in the coals and process residues

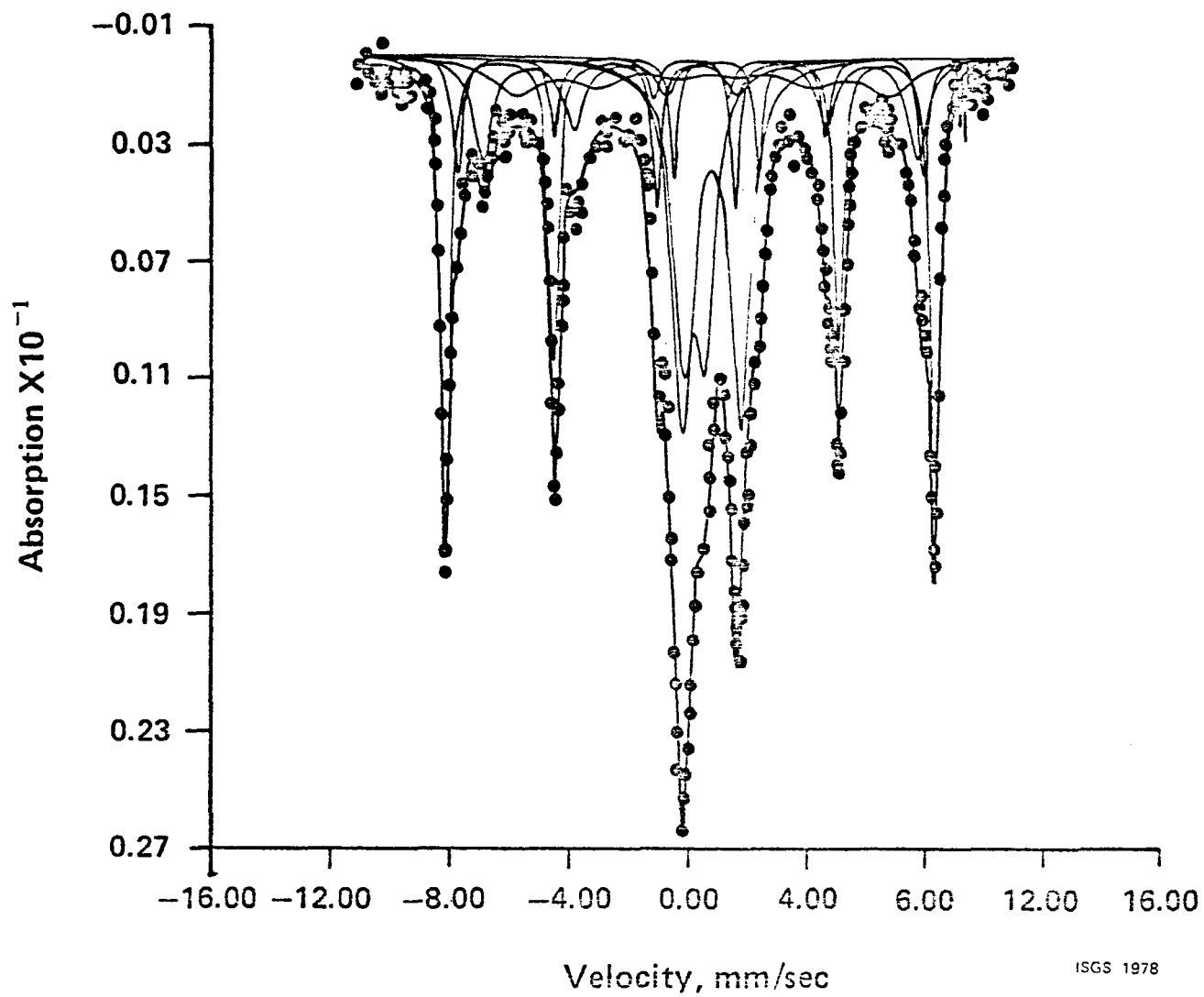
	IL No.5 Coal	IL No.6 Coal	Low-sulfur refuse gob	High-sulfur refuse gob	Slurry washed fines	Medium temp. char	High temp. char	H-Coal ^(R)	SRC residue	Lurgi Ash	Fly Ash conventional power plant
Pyrite	X	X	X	X	X	X	X		X		
Pyrrhotite						X	X	X	X		
Illite	X	X	X	X	X	X					
Mullite							X			X	X
Melanterite			X								
Fe ⁺² silicate										X	X
Hematite										X	X
Goethite										X	X
Magnetite										X	X
Hydrated iron sulfates	X			X	X	X	X	X	X		



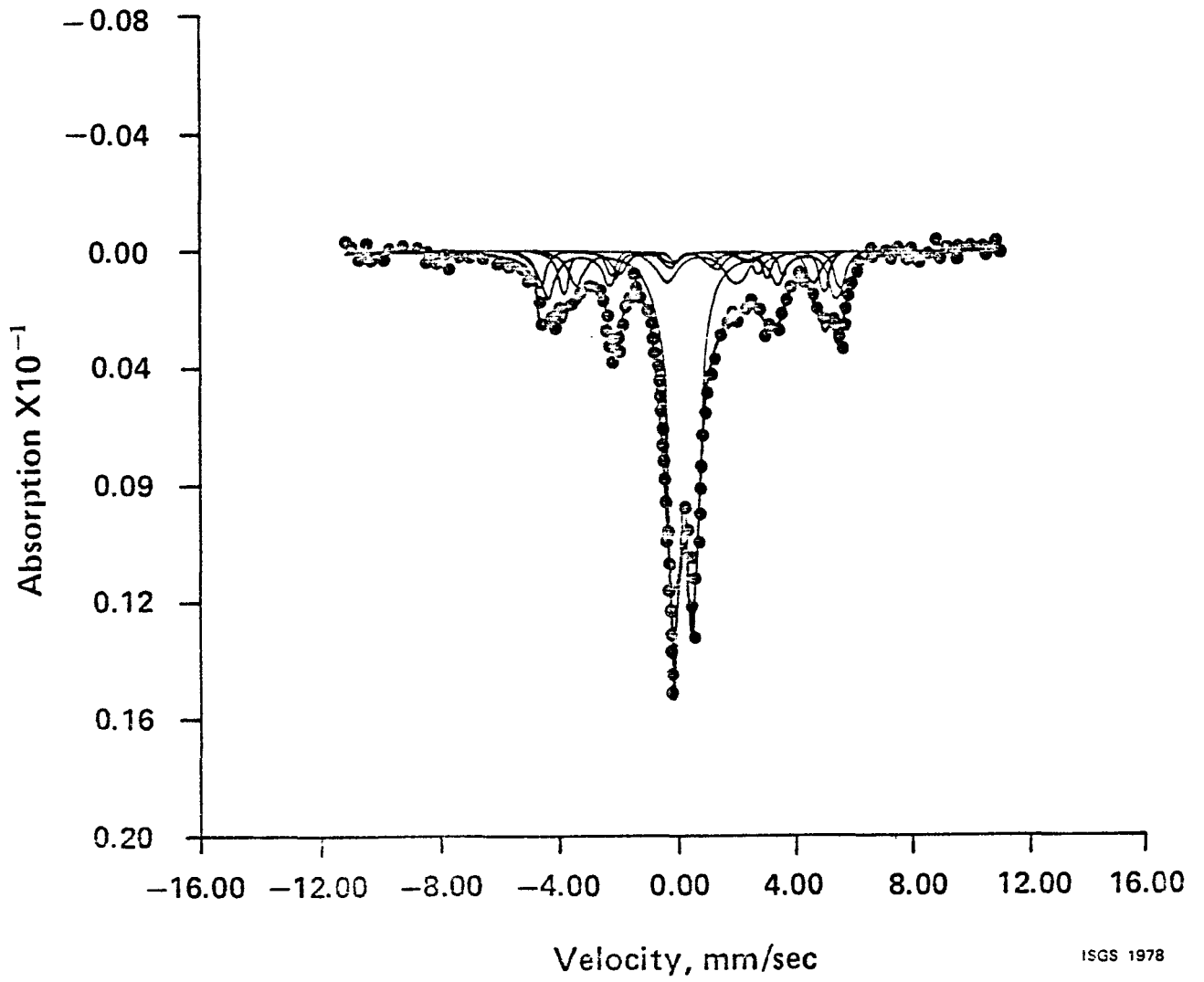


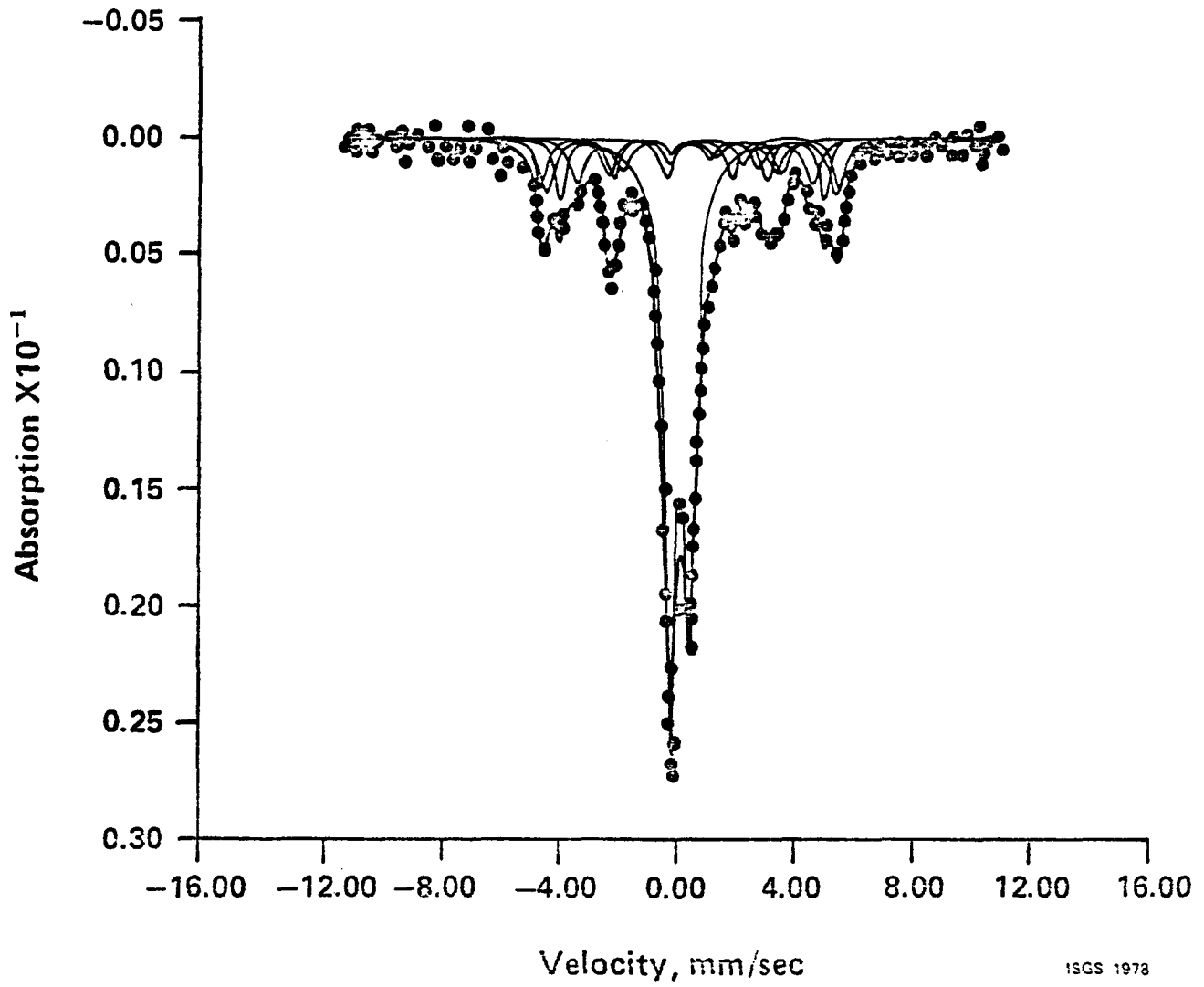
ISGS 1978

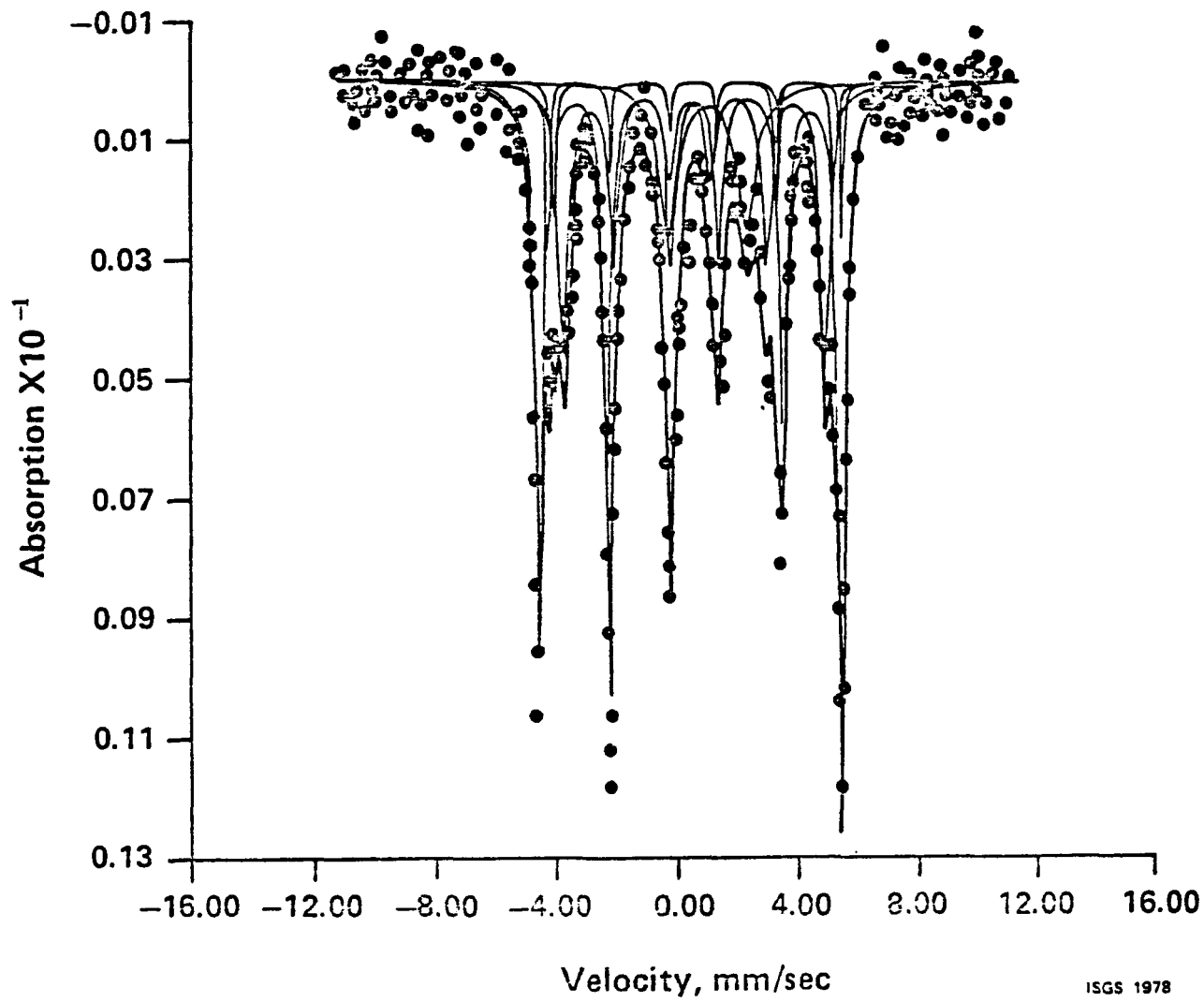




ISGS 1978







A P P E N D I X E
IDENTIFICATION OF POTENTIAL POLLUTANTS
FROM COAL CONVERSION WASTES

IDENTIFICATION OF POTENTIAL POLLUTANTS FROM
COAL CONVERSION WASTES

by

R. M. Schuller, J. J. Suloway, R. A. Griffin, S. J. Russell,
and W. F. Childers

A paper presented at the Society of Mining Engineers-American
Institute of Mining Engineers (Littleton, Colorado) Annual
Meeting, February 18-22, 1979, New Orleans, Louisiana.

IDENTIFICATION OF POTENTIAL POLLUTANTS FROM COAL CONVERSION WASTES

R. M. Schuller¹, J. J. Suloway², R. A. Griffin¹, S. J. Russell¹, and W. F. Childers²

¹Illinois State Geological Survey
²Illinois State Natural History Survey
Urbana, Illinois

ABSTRACT

Seven solid wastes from coal conversion processes were characterized chemically and mineralogically. The wastes included three LURGI gasification ashes, two liquefaction residues (SRC and H-coal), a fly ash, and a water-quenched slag. Leachates generated from the solid wastes at various pH levels over the range 2.5 to 11.0 were analyzed for over 40 constituents. Results of the leachate analyses demonstrate the wide variation in constituent solubility for the solid wastes. To help assess the environmental impact of the disposal of these wastes, the leachates were also employed in soil attenuation studies and acute 96-hour static bioassays using young fathead minnows.

INTRODUCTION

Coal is the most abundant fossil fuel in the United States. As the demand for energy increases and the supply of energy from other sources decreases, coal will become an increasingly important energy source to our nation. However, due to impurities in the coal that could result in possible pollution of the environment, not all of the available coal will be used directly for energy production. Large reserves of high sulfur coal make the development of a coal conversion industry likely, but the production of clean fuel from coal by liquefaction and gasification processes is not without its potential environmental impacts. Among these impacts are the large amount of solid wastes generated and the associated disposal problems. The assessment of potential impacts of the solid wastes generated from both coal conversion and coal-fired power plants on the quality of water resources is underway at the Illinois State Geological Survey and the Illinois Natural History Survey (1,2).

In order to evaluate the potential environmental impacts of coal solid wastes it is necessary (1) to characterize the solid wastes, both chemically and mineralogically, (2) to chemically characterize the leachate generated from the solid waste, (3) to determine the attenuating nature of earth materials with which the leachate may come into contact, and (4) to determine the toxicity to biota from the resulting leachate.

Because this report is being published before the completion of the entire project, the authors reserve the right to revise interpretation of data upon completion of the project.

IDENTIFICATION OF POTENTIAL POLLUTANTS

Chemical and Mineralogical Characterization

The seven wastes reported here, along with their feed coals and the processes used to generate the solid wastes, are listed in Table 1. Included are three ashes from the LURGI gasification process employing three different feed coals; two liquefaction residues, H-coal and SRC; and two power plant wastes, a fly ash and a water-quenched bottom slag.

The chemical composition of the solid wastes was determined for over 60 constituents. The major constituents and their percentages of the waste are listed in Table 2. Additional constituents typically found in concentrations greater than 100 mg/kg included: B, Ba, Cr, F, Mn, Sr, Zn, and Zr. An additional 20 elements were found in detectable concentrations less than 100 mg/kg.

Samples of three coals and the solid wastes were analyzed by both Mössbauer spectroscopy and X-ray diffraction to determine their mineralogy and are reported in Tables 3 and 4. The minerals identified in the solid wastes are listed in Table 4, except for the slag, which was an amorphous silica (glass). No X-ray diffraction peaks were given by the slag, and Mössbauer analysis yielded only five unidentified Fe species that were probably iron-silicates of varying composition.

Comparison of Tables 3 and 4 indicates that several minerals participate in chemical reactions during coal conversion processes. For example, pyrite is the dominant form of iron in the feed coals, but is almost totally converted to hematite during the LURGI gasification process and during combustion to form the fly ash. In contrast, during the H-coal liquefaction process, the pyrite was converted to pyrrhotite and troilite (3).

Aqueous Solubility

To determine the soluble constituents of the solid wastes, 10 percent aqueous slurries of each waste were made. The slurries were set up in series of four and adjusted to pH values over the range 2 to 11. The pH values of the slurries were monitored and readjusted to the specified values when necessary. Chemical equilibrium was assumed when the pH remained constant. The period for achieving equilibrium lasted 3 to 6 months. However, studies conducted with the LURGI ashes indicated that equilibrium of over 90 percent was attained within one week. Duplicate sets of the slurries were made. One set was equilibrated under an argon (oxygen- and CO₂-free) atmosphere and the other under an air atmosphere.

Table 1: Sources of the solid wastes

Sample	Coal	Process
1. LURGI Ash	Illinois Herrin #6	LURGI gasification (Westfield, Scotland)
2. LURGI Ash	Illinois #5	LURGI gasification (Westfield, Scotland)
3. LURGI Ash	Big Sky (Montana)	LURGI gasification (Westfield, Scotland)
4. SRC	Kentucky #9 Coal	Liquefaction dry mineral residue
5. H-Coal	Illinois Herrin #6	Liquefaction mineral residue (vacuum still bottoms)
6. Fly Ash	Illinois Herrin #6	power plant
7. Slag	Illinois Herrin #6	power plant (water quenched)

Table 2: Major elemental composition of the solid wastes

Element	Solid Waste (%)						
	LURGI #5	LURGI #6	LURGI Big Sky	H-Coal	SRC	Fly Ash	Slag
Al	9.6	10.8	10.1	1.7	6.7	7.4	8.5
Ca	2.3	1.7	6.0	0.8	0.8	2.6	4.4
Fe	15.1	14.4	6.0	2.4	13.5	13.4	13.7
K	1.3	1.5	0.5	0.2	0.9	2.1	1.3
Mg	0.4	0.4	2.2	<.1	<.1	.35	0.5
Na	0.2	0.2	<.1	<.1	0.1	1.3	0.6
S	0.5	0.6	0.5	1.8	8.2	1.5	0.1
Si	24.6	23.0	22.6	4.0	11.1	19.4	22.3
Ti	0.6	0.6	0.6	0.1	0.2	.5	0.4

Table 3: Mineral composition of Illinois No. 5 (IL 5), Illinois No. 6 (IL 6), and Montana Big Sky seam coals

Minerals Identified	IL 5	IL 6	Big Sky
Pyrite (FeS_2)	X	X	X
Sphalerite (ZnS)	X	X	
Melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$)			X
Goethite ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$)			X
Quartz (SiO_2)	X	X	X
Cristobalite (SiO_2)			X
Calcite (CaCO_3)	X	X	X
Dolomite (Ca-MgCO_3)			
Anhydrite (CaSO_4)	X	X	X
Bassinite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$)			X
Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)			X
Illite (Al-silicate clay)	X	X	X
Kaolinite (Al-silicate clay)	X	X	X
Expandable clays (Montmorillonite, etc.)	X	X	X

NOTE: All minerals identified by X-ray diffraction; Mossbauer analysis also confirmed pyrite and illite.

The leachates from the wastes were analyzed for 43 constituents, and these concentrations were compared to recommended water quality levels (4). The analyses were performed by atomic absorption and colorimetric techniques (5). Table 5 lists those constituents found to exceed the recommended levels over the pH range studied and under the laboratory conditions described above. Although many constituents exceed the recommended levels under acid conditions, those that exceed the recommended levels over the entire pH range are felt to represent the highest potential for pollution. Also given in Table 5 are the pH ranges of the leachates employed and the pH values of the two natural pH solutions for each aerobic and anerobic set of slurries for each waste. The natural pH slurries are those that were allowed to equilibrate without pH adjustment by addition of either nitric acid or sodium hydroxide. Table 5 indicates that there is a strong similarity between the soluble constituents found in a solid waste and the treatment that it undergoes, i.e., the 3 LURGI ashes yielded nearly the same major soluble constituents for all three feed coals employed. The same was true for the two liquefaction wastes. The Illinois #6 coal was used in both the LURGI and H-coal processes but resulted in the derivation of quite different soluble constituents from their wastes.

Table 4: Minerals identified in several coal conversion solid wastes

Minerals Identified	LURGI			H-Coal	SRC	Fly Ash
	LURGI Ash IL 5	LURGI Ash IL 6	LURGI Ash Big Sky			
Hematite (Fe ₂ O ₃)	X	X	X			X
Magnetite (Fe ₃ O ₄)	X	X	X			X
Pyrrhotite (Fe _{1-x} S)				X	X	
Troilite (FeS)				X		
Sphalerite (ZnS)				X		
Fe ⁺³ -clay	X	X	X			
Fe ⁺² -silicate	X	X	X			
Quartz (SiO ₂)	X	X	X	X	X	X
Plagioclase Feldspar Na(AlSi ₃ O ₈) - Ca(Al ₂ SiO ₈)	X	X	X			
Wollastonite (CaSiO ₃)				X		
Dolomite (Ca-MgCO ₃)						
Calcite (CaCO ₃)				X		X
Gypsum (CaSO ₄ · 2H ₂ O)	X	X	X			
Anhydrite (CaSO ₄)				X		X
Pyrolusite (MnO ₂)	X	X	X			
Mullite (3Al ₂ O ₃ · 2SiO ₂)	X	X	X			
Illite (clay)				X	X	
Kaolinite (clay)				X	X	
Expandable clays (Montmorillonite, etc.)				X	X	

The K, Mn, Na, and Sb found in the LURGI ash leachate are not as soluble as constituents in the leachate from the H-coal residue under the conditions employed.

Attenuation Analyses

The next step in identifying the potential pollutants from coal processing wastes was to determine the interaction of the waste leachates with earth materials and to extrapolate the results to the land disposal of these wastes. A batch reactor technique was employed for the analyses. The technique involves mixing a known volume of leachate with a known weight of soil. This process is repeated five times in series, with portions of leachate being drawn off and filtered for analysis. Additional details of that technique and rationale for using this methodology are given elsewhere (2,6).

Three Illinois soils, Ava silty clay (sicl), Catlin silt loam (sil), and Bloomfield loamy sand (ls), each having a broad range of physical and chemical characteristics, were collected and characterized for the study. Table 6 gives some of the pertinent chemical and physical parameters of these soils. The filtrates collected were analyzed for Al, B, Ca, Fe, K, Mg, Mn, Na, SO₄, and Zn. These constituents were determined because of their presence in the leachates in amounts that might constitute a pollution hazard due to leaching through soil.

Table 7 summarizes the behavior of the constituents in the waste-leachate/soil mixtures. Generally, the attenuation of constituents in each leachate was similar for each soil type, although the degree of removal or elution of individual constituents varied with soil type. From this investigation, Mg stands out as the most likely potential pollutant from land disposal of

Table 5: Constituents with concentrations exceeding recommended water quality levels under the laboratory test conditions.

Sample	Natural pH			Constituent
	aerobic	anerobic	pH range	
LURGI Ash Illinois #6 Coal	7.6	8.9	8.9-2.7	B, Ca, K, Mn, Na, NH ₄ , SO ₄ , Sb
LURGI Ash Illinois #5 Coal	8.3	10.9	10.9-3.1	B, Ca, K, Na, NH ₄ , Pb, SO ₄ , Sb
LURGI Ash Big Sky Coal	8.5	11.1	11.1-3.1	B, Ca, Cd, K, NH ₄ , Pb, SO ₄ , Sb
SRC	6.4	7.5	10.2-2.9	B, Ca, NH ₄ , SO ₄
H-Coal	8.8	11.3	11.3-2.3	B, Ca, NH ₄ , SO ₄
Slag	3.8	5.7	9.9-2.8	NH ₄
Fly Ash	4.1	4.3	10.0-2.5	B, Ca, SO ₄

the coal processing wastes. Comparison of the original leachate concentration of Mg to the concentration of Mg in the filtrate from the mixtures shows as much as a 20-fold increase. These final filtrate concentrations were quite often in the range of 150 to 300 mg/L. This is believed to be due to cation-exchange reactions in the soil and has been found to cause increases in hardness of ground waters around waste disposal sites similar to those envisioned for the disposal of coal conversion wastes (1).

Figures 1 through 4 are plots of concentrations of individual leachate components vs. soil/leachate ratios for several of the wastes. This type of plot can be used to illustrate which soils are most effective at removing a given constituent from a given leachate. Figures 1 and 2 show the rates of removal of Zn and Fe from two waste leachates. Catlin soil proved to be the most efficient of the three soils tested in removing metals from solution. This is probably due to its higher cation-exchange capacity and its higher pH (7.1). The higher exchange capacity of the Catlin soil neutralizes acidity better than the other two soils due to its higher buffering capacity and in many cases results in precipitation of metal hydroxides.

Under the conditions employed, boron exceeds the recommended water quality levels in all of the waste leachates except the water-quenched slag. Its concentration ranges from 5 ppm to as high as 65 ppm (LURGI Ash, Big Sky Coal) in the leachates. Figure 3 typifies the plot of B removal from solution with Catlin being most efficient followed by Ava and Bloomfield, respectively. Although the mechanism for B removal has not yet been interpreted, its more gradual removal rate may indicate that dilution due to soil water may be partially responsible. Other workers have shown that boron is readily adsorbed by illite clay (7,8) and that adsorption increases with increasing pH (9). Both these factors favor higher retention of boron by the Catlin soil than by the Ava or Bloomfield soils.

Magnesium, as stated above, may well be the greatest problem as a possible pollutant from the disposal of the solid wastes. Figure 4 shows the elution of Mg from Catlin and Ava soils after mixing with the acid SRC leachate. In this instance Bloomfield was not a source of Mg elution. However, in other cases it does elute Mg, but not to the extent that the other two soils do.

Figures such as those shown here can be used to determine the migration distance of a soluble constituent with time. Figure 1 is a plot of the zinc concentration vs. the soil/leachate ratio for the Fly Ash leachate (pH 4.1). The initial step is to determine graphically the soil/leachate ratio needed to obtain the desired water quality level for the element of interest; in this case for zinc the drinking water standard of 5.0 ppm is used. For the Ava soil, the ratio equals 0.75 g/mL. This means that 0.75 g of soil for each mL of leachate is needed to reduce the initial zinc concentration of the leachate down to the drinking water standard. It is then necessary to determine the volume of leachate to be generated per unit time and the soil bulk density. From this data the migration distance per unit time can be computed.

If it is assumed that:

soil bulk density = 1.50 g/cm³
 leachate volume = 6 inches/yr (15.24 mL/cm²/yr)
 landfill life = 30 years

the migration distance is computed to be:

$$\frac{(0.75 \text{ g/mL})(15.24 \text{ mL/cm}^2/\text{yr})(30 \text{ years})}{1.50 \text{ g/cm}^3} = 228 \text{ cm or } 7.5 \text{ ft in } 30 \text{ years.}$$

Toxicity Study

Toxicity tests were conducted in conjunction with the physical and chemical analyses of the coal conversion wastes and their leachates. The purpose of the toxicity testing was to determine whether or not the leachates generated from the coal conversion solid wastes were acutely toxic to aquatic organisms. Ninety-six hour static bioassays were conducted with one-to-six-day-old fathead minnows (*Pimephales promelas*) to determine the acute toxicity of the waste leachates. The bioassays were conducted as previously reported by Griffin et al. (3) in accordance with procedures outlined in "Methods for Acute Toxicity Tests with Fish, Macroinvertebrates, and Amphibians" (10).

Table 6: Characteristics of the soils employed in the attenuation analysis

Soil	pH	CEC (meq/100g)	Surface Area, N ₂ (m ² /g)	Organic Carbon (%)	Sand (%)	Silt (%)	Clay (%)
Catlin silt loam	7.1	18.1	10.1	4.73	11.6	60.9	27.2
Ava silty clay loam	4.5	13.1	28.3	1.18	2	69.6	28.4
Bloomfield loamy sand	5.7	0.8	1.7	0.21	82	10	8

Table 7: Summary of soil-attenuation behavior of chemical constituents in leachates from several coal solid wastes

Elements	
Al, B, Ca,	
Total Fe,	attenuated
Na*, SO ₄ , Zn,	
Additional trace metals	
K*	variable
Mg	eluted
Mn	pH dependent variability

*eluted or steady at low concentrations (<10 ppm).

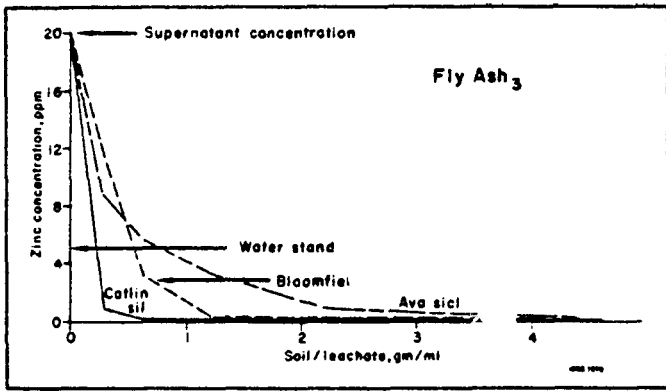


FIGURE 1. Zinc concentration vs. soil/leachate ratio for Fly Ash₃ (pH 4.12).

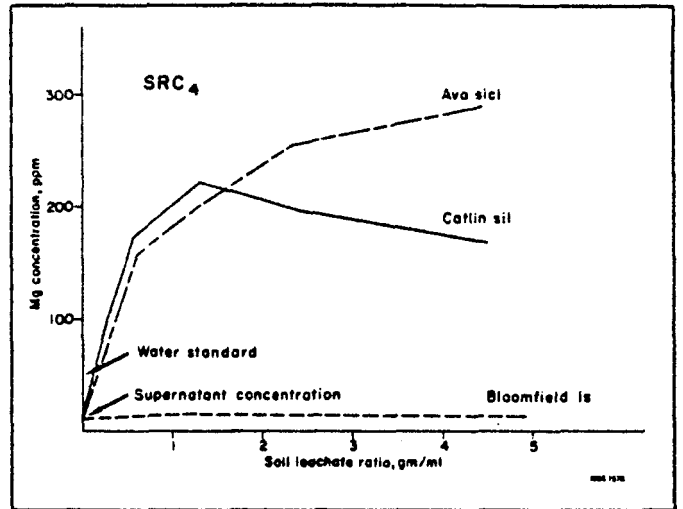


FIGURE 4. Mg concentration vs. soil/leachate ratio for SRC (leachate pH 3.5).

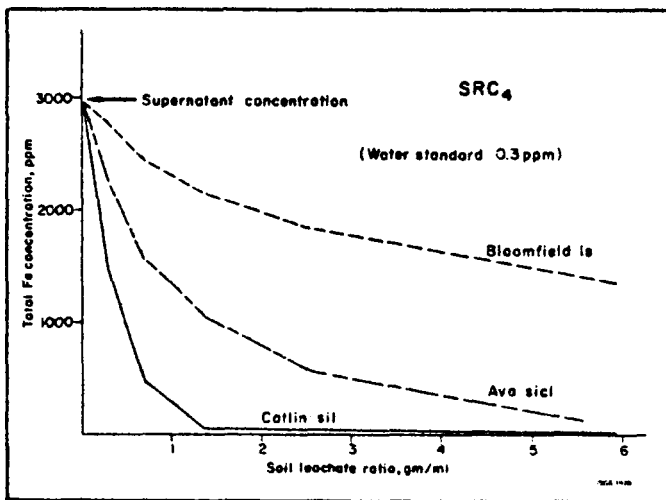


FIGURE 2. Total Fe concentration vs. soil/leachate ratio for SRC (leachate pH 3.5).

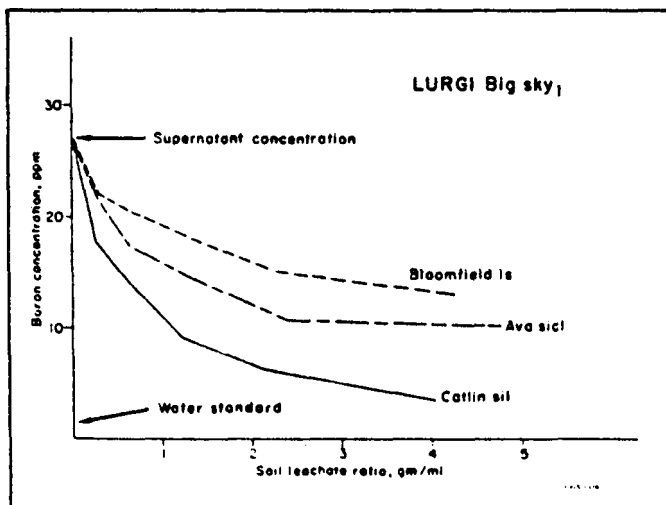


FIGURE 3. Boron concentration vs. soil/leachate ratio for LURGI Big Sky (leachate pH 8.4).

The results of the screening procedures are depicted in Figure 5. Generally, leachates of neutral pH (6.6 - 8.8) were relatively nontoxic. Total mortality occurred at extreme pHs (pH <6.1 and pH >10.0) and was partially due to "ionic shock." With increasing acidity, there was an increase in toxicity and a decrease in the LC-50 value. The natural pH leachates from the LURGI process were not acutely toxic. The natural pH leachate generated from H-Coal residue under an aerobic atmosphere was relatively nontoxic. However, the natural pH leachate equilibrated under anaerobic conditions was very alkaline (pH = 8.8), and 35 percent mortality occurred during the screening procedure. To ensure survival, a 1:2 dilution was required. During the screening procedure, total mortality occurred in the aerobic natural pH leachate from SRC. This leachate was acidic (pH = 5.6), and a 1:10 dilution was required to ensure survival. The natural pH leachate of SRC equilibrated under anaerobic conditions was a neutral solution; however, 45 percent mortality occurred in the screening procedure. Natural pH leachates generated from the slag and fly ash were very acidic (pH <5.9), and large amounts of dilution (>1:5) were required to ensure survival.

Many factors probably contributed to the acute toxicity of the acidic leachates. We have demonstrated (3) that total mortality occurs when fathead minnow fry are exposed to acidic reconstituted water (pH <5.9) for 96 hours. Since the test organisms were propagated and held in water having a pH of 7.4 and experienced a rapid change in pH, the mortality was partially due to "ionic shock." Some of the acidic leachates also contained concentrations of Al, Cr, Cu, Mg, Ni, and Zn which, under laboratory conditions, have been shown to be acutely toxic to fish (11-16). Because of the complexity of the chemical composition of the leachates and the unknown synergistic and antagonistic effects of the chemical constituents composing the leachates, it was not possible from these experiments to determine which specific chemical constituents were directly responsible for the observed mortality that occurred in some leachates of neutral pH.

SUMMARY

The identification of potential trace element pollutants from coal conversion wastes is of concern because of the enormous quantity of waste that may be generated. In order to evaluate this potential, it is necessary to characterize both the solid waste and the leachate that the waste is capable of generating. It is then necessary to determine how the constituents are removed and attenuated from the leachate by soil materials and how these constituents will affect the biota if they are not removed or attenuated.

Analysis of the seven coal conversion wastes has shown that:

- (1) several minerals participate in chemical reactions during conversion;
- (2) the soluble constituents in a solid waste from coal conversion may be a function more of the process than of the feed coal;
- (3) while most chemical constituents in the leachates were attenuated by the soils employed in this study, the elution of Mg and Mn from the soils may represent the greatest potential threat as an environmental contaminant; and
- (4) the bioassays indicated that most of the leachates were not acutely toxic under neutral pH conditions; however, the leachate generated from SRC dry mineral residues was acutely toxic under neutral conditions. The SRC waste, along with the fly ash and slag, whose natural pH leachates were acidic, poses the greatest potential environmental hazard to the biota.

ACKNOWLEDGMENTS

We gratefully acknowledge the U. S. Environmental Protection Agency, Energy Assessment and Control Division, Fuel Process Branch, Research Triangle Park, North Carolina, for partial support of this work under Contract 68-02-2130, Characterization of Coal and Coal Residue.

The authors wish to thank the Analytical Chemistry Section of the Illinois State Geological Survey under the direction of R. R. Ruch and to thank N. F. Shimp, R. W. Ringler, and H. D. Glass for assistance in portions of this research. The authors are indebted to G. V. Smith, C. C. Hinckley, and M. Saporoschenko of the Coal Extraction and Utilization Research Center, Southern Illinois University, Carbondale for Mossbauer Spectroscopic Analyses of the samples.

REFERENCES

1. Griffin, R. A., et al., Illinois State Geological Survey, Environmental Geology Note 78 (1976).
2. Schuller, R. M., R. A. Griffin, and J. J. Suloway, "Chemical and Biological Characterization of Leachate from Coal Cleaning Wastes," EPA Symposium on Coal Cleaning to Achieve Energy and Environmental Goals (1978).
3. Griffin, R. A., R. M. Schuller, J. J. Suloway, S. J. Russell, W. F. Childers, and N. F. Shimp, "Solubility and Toxicity of Potential Pollutants in Solid Coal Wastes," EPA-600/7-78-063, Environmental Protection Technology Series (1978).

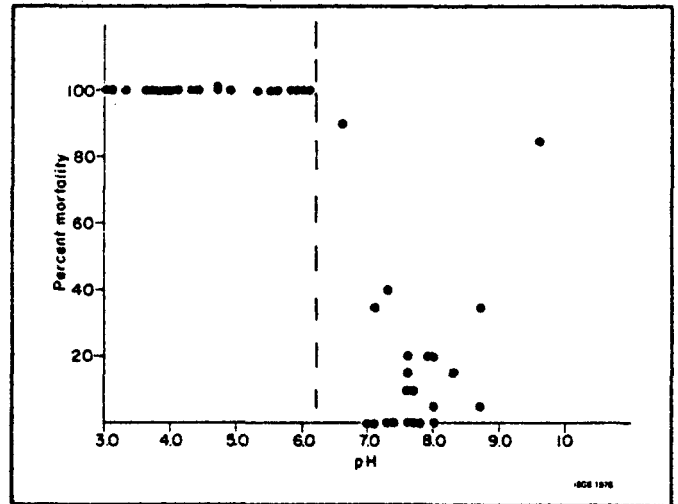


FIGURE 5. The percentage of mortality of one-to-six-day-old fathead minnow fry (*Pimephales promelas*) resulting from 96-hr exposures to 56 leachates of different pHs generated from seven coal solid wastes.

4. Environmental Protection Agency, "1972 Water Quality Criteria," U. S. EPA, R3-73-033, Washington, D. C. (1972).
5. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-625/5-74-003 (1974).
6. Rovers, F. A., H. Mooij, and G. J. Farquhar, "Contaminant Attenuation - Dispersed Soil Studies," EPA-600/9-76-015 (1976).
7. Harder, H., "Incorporation of boron in detrital clay minerals," *Geochemica et Cosmochemica Acta* 21: 284-294 (1961).
8. Couch, E. L., and R. E. Grim, "Boron fixation by illites," *Clays and Clay Minerals* 16:249-255 (1968).
9. Sims, J. R., and F. T. Bingham, "Retention of boron by layer silicates, sesquioxides, and soil materials: I. Layer silicates," *Soil Sciences Society of America Proceedings* 31:728-731 (1967).
10. Committee on Methods for Toxicity Tests with Aquatic Organisms, "Methods for Acute Toxicity Tests with Fish, Macroinvertebrates, and Amphibians," Ecology Research Series, EPA-600/3-75-009, U. S. EPA, Corvallis, Oregon (1975).
11. Brown, V. M., "The Calculation of the Acute Toxicity of Mixtures of Poisons to Rainbow Trout," *Water Research* 2:723-733 (1968).
12. Doudoroff, P., and M. Katz, "Critical Review of Literature on the Toxicity of Industrial Wastes and Their Components to Fish. II. The Metals, as Salts," *Sewage and Industrial Wastes* 25:802-839 (1953).
13. Eaton, J. G., "Chronic Toxicity of Copper, Cadmium and Zinc Mixture to the Fathead Minnow (*Pimephales promelas*)," *Water Research* 7:1723-1736 (1973).

14. Pickering, Q. H., "Chronic Toxicity of Nickel to the Fathead Minnow," Journal of the Water Pollution Control Federation 46:760-766 (1974).

15. Pickering, Q. H., and M. H. Gast, "Acute and Chronic Toxicity of Cadmium to the Fathead Minnow, Pimephales promelas," Journal of Fisheries Research Board of Canada 29:1099-1106 (1972).

16. McCarty, L. S., J. A. C. Henry, and A. H. Houston, "Toxicity of Cadmium to Goldfish, Carassius auratus, in Hard and Soft Water," Journal of Fisheries Research Board of Canada 35:35-42 (1978).